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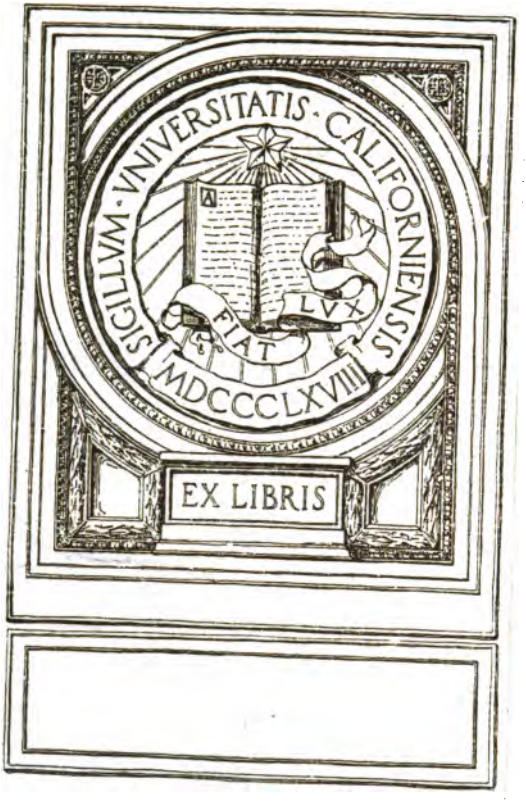
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THE CHEMISTRY OF THE RUBBER INDUSTRY

OUTLINES OF INDUSTRIAL CHEMISTRY.

A Series of Text-books Introductory to the Chemistry of the National Industries.

EDITED BY

Guy D. Bengough, M.A., M.Sc.

OUTLINES OF INDUSTRIAL CHEMISTRY.

THE CHEMISTRY

OF THE

RUBBER INDUSTRY

BY

HAROLD E. POTTS, M.Sc.

(of the firm of Hubers and Mond)

Member International Rubber Testing Committee

Univ of California

NEW YORK

D. VAN NOSTRAND COMPANY

23 MURRAY AND 27 WARREN STREETS

1912

TS1892
P6D

UNIV. OF
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GENERAL PREFACE TO THE SERIES

THE object of the series of volumes collected together under the general title "Outlines of Industrial Chemistry" is to provide students and persons employed on the technical side of any particular industry with a handbook explaining the chemical aspect of the operations carried on in that industry. It is hoped, too, that the series may be found useful and interesting to many business heads and subordinates who are employed mainly in the office, but who still take an interest in the processes by which their dividends or salaries are earned.

Only a slight acquaintance with chemistry is assumed on the part of the reader; in fact, a principal object of the series is to provide a link between the elementary chemistry taught in schools and institutions which provide instruction up to, say, the matriculation standard of a modern university, and the larger text-books dealing with the details of the separate industries. In most cases these large works are quite beyond the intellectual and financial reach of those who enter industrial employment, and the result is that a clear understanding of the essential processes of an industry can only be obtained by slow absorption from the busy senior members of the staff.

It is believed, moreover, that each volume in the series, though it deal with the chemistry of one industry only, will serve an educational as well as a purely utilitarian purpose. Examples which illustrate the general processes of deduction, and of the building up of an hypothesis or theory by the scientific method, may be drawn from the particular set of chemical facts to be

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met with in almost any one industry. Thus, while familiarising himself with just those phenomena which are of fundamental importance to him, the student will be learning how they may be correlated and welded together into a coherent scientific system.

The science of chemistry has grown so rapidly in recent years, and such immense masses of knowledge have been accumulated, that no one man can hope to become even moderately conversant with every branch of the subject. A student possessing an elementary general knowledge of chemistry, and only a limited time for study, is therefore justified, even from an educational point of view, in spending that time in the study of the class of facts most intimately associated with his particular industry.

Such a course has the further advantage that it will stimulate the best intellects to seek for a deeper knowledge of pure chemistry. A thinking student will soon find that he has come face to face with phenomena which he cannot explain in the light of the knowledge he has already acquired. He will feel that progress in the chemical side of his industry may very possibly be obtained by careful investigation of the unexplained and unexpected anomalies that occur from time to time; or, perhaps, by the application or adaptation of principles or processes discovered by purely scientific workers in the laboratory. In this way he may be brought back to study more deeply the methods and principles of pure chemistry; such a study can but react to the benefit of the student, the employer and the industry concerned.

GUY D. BENGOUGH

AUTHOR'S PREFACE

This book aims at bridging the gap between pure chemistry and manufacturing practice. It is intended to explain to the chemist who wishes to work on rubber the chief properties of the material with which he has to deal, and the chief lines on which his work may run. It is also intended to explain to the rubber technologist the nature of the problems with which a rubber chemist is concerned, and to make clear the difficulties, but also the possibilities, of chemical routine and research. In short, the object is to exhibit the points of contact between Chemistry and the Industry.

It has been considered advisable to begin with a chapter on Colloidal Chemistry, since some knowledge of this subject is a necessary part of the equipment of the chemist who wishes to understand modern views on almost any rubber problems.

The production and manufacture of rubber have then been considered, not for the sake of their own technique but for their bearing on chemical work. Lastly, the analytical processes of most importance have been critically described and explained. It may be added that illustrations of rubber machinery are not given, as not being consonant with this plan. Those who wish to see such illustrations will find them in abundance, not merely in works on the subject, but also in the advertisement pages of the technical press.

A few references have been given in the text. References to

books, to some of which I am indebted, occur at the end of each chapter.

I have to thank the Editors of the *Journal of the Society of Chemical Industry*, the *India Rubber Journal*, and the *Rubber World* for permission to utilise matter contributed to their columns by myself and by others. I also wish to thank Mr. W. J. Britland and Miss E. M. Parrington, B.Sc., who have assisted me in reading the proofs.

H. E. POTTS.

19, SOUTHAMPTON BUILDINGS,
CHANCERY LANE,
LONDON, W.C.
Nov., 1911.

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THE CHEMISTRY OF THE RUBBER INDUSTRY

CHAPTER I

THE COLLOIDAL STATE

RUBBER is a substance obtained from the milk or latex of various trees, in which it occurs in the form of an emulsion. As it is one of the large and important class of bodies known as the colloids it is necessary to give a short account of the properties of both colloids and emulsions before attempting any discussion of the chemistry of rubber itself.

The definition of a certain class of substances as colloids was due to the researches of Thomas Graham. In an important paper read before the Royal Society, entitled "Liquid Diffusion applied to Analysis," he showed that substances could be divided into two classes according to the behaviour which they exhibited when their aqueous solution was placed in a parchment membrane surrounded by pure water. The substances which were found to diffuse through the wall of parchment into the water were termed "crystalloids," while those which did not possess this property were termed "colloids." Salts and other crystallisable substances belonged to the crystalloid class. The term colloid is derived from the Greek, signifying glue, because many members of this class resemble glue in some respects. This difference in behaviour in the presence of a parchment membrane is one of the most important distinctions between colloids and crystalloids. It will, however, be more in accordance with the principles of modern teaching to define colloids in a manner which will bring out as far as possible their points of resemblance with other substances, rather than those of dissimilarity. The whole trend

of investigation now appears to lead to the conclusion that there are very rarely sharp distinctions in Nature, but that there are usually smooth transitions between even the most dissimilar types of substances and of phenomena.

Indeed, it may almost be said now that to the eye of the colloidal chemist there need be no sudden gap in properties in passing between systems so diverse as the wet sand on the beach and the salt water in the sea. This difference is so great when viewed in the light of ordinary chemical concepts that it will be profitable to consider this case in detail, since in this way it will be possible to gain an insight into some of the more striking characteristic properties of the colloidal state.

The first and most evident difference then is that wet sand is a system of two phases, sand and water, while salt water is a system in which only one phase is present, a solution of salt. In each case a phase means a portion of matter which is alike throughout and is separated in space from other portions of matter of a different kind. Although salt water contains two different substances, it is called a phase because the salt is distributed throughout the water in a uniform manner, since even with the aid of the most refined methods we are unable to discover any difference between portions of the solution, however finely we may divide it, unless chemical decomposition occurs. In a word, salt solution is homogeneous—equal in properties throughout.

In the case of wet sand this is obviously not so. Two phases are clearly present which may be separated by the crudest mechanical means such as filtration or even decantation. The system is heterogeneous—unequal in properties throughout. This difference comes about because the salt in salt water is present in the form of molecules, which are smaller than half the wave length of light, and consequently are invisible. The sand particles, on the other hand, consist of aggregations of many molecules, which attain a size such that they are readily visible.

We may now consider the effect of increasing the size of the molecules which are invisible in the case of salt, or of breaking down the groups of molecules which are easily visible in the case

of silica. In this way we shall reach in either case an intermediate system which will possess remarkable properties. In attempting to bridge over the gap between these two systems we will start from each end and gradually modify the properties, in particular the size of the molecule, in order to arrive at an intermediate system which will resemble both. It will be seen that new and surprising properties will develop, and in this way we shall be led to a definition of the colloidal state.

Beginning with wet sand, the most obvious method of obtaining simpler molecular groups of silica is to pulverise the sand. In this way a very fine state of division may be attained, so that if more water is added the sand requires a long time to settle out after shaking. A suspension of sand in water has been made. The length of time required for settling increases as the sand becomes more finely divided. Exhaustive researches on this point have been carried out by Schneider and Barus, who examined the velocity of sedimentation (settling) of suspensions of clay in water. More recently Spring has observed very interesting phenomena in the case of suspensions of lamp-black in water. The suspension formed by shaking lamp-black with water was not very stable. It settled out on standing, and the lamp-black could be separated by filtration. When the lamp-black was shaken with a ½ per cent. solution of soap, a suspension of extraordinary stability was obtained, which did not settle out even on standing for weeks. On attempting to filter the liquid it was found that the carbon ran through the filter. As a curious illustration of the complexities of the subject, it may be mentioned that with a 2 per cent. soap solution the suspension settled out almost as rapidly as with pure water.

In these cases the state of subdivision of the suspended substance is still excessively coarse when estimated from a molecular point of view. To obtain suspensions in which the particles are of a much finer grain, recourse must be had to methods of pulverisation other than mechanical ones. A suitable refinement for the purpose in view consists in the employment of electrical shattering of the substance. A large volume of work has recently been performed by Bredig and Svedberg with various metals, which have been obtained in a state of extremely fine

suspension in water and many organic liquids. The method adopted by Bredig was very simple, consisting in the passage of an electric arc between poles of the metal immersed in the liquid. In this way a powerful shattering or disintegrating effect was secured, and the metal was deposited as an excessively fine dust, which remained suspended in the liquid when the voltage was fixed at the right strength. The method is really an extension of the long-known fact that when an arc is made between metallic poles in air the metal is deposited as an exceedingly fine dust. The method worked out by Svedberg for an extensive range of metals in a large number of liquids, especially water and various alcohols, depends on the passage of a current between poles of some metal which is not easily shattered, such as aluminium or iron ; these dip in the desired liquid on either side of pieces of foil of the metal which is to be shattered. By these methods the metal can be so finely divided that the liquid appears homogeneous to the eye. The alkali metals yield beautifully-coloured liquids in alcohol and ether by the Svedberg method, and many other metals behave similarly.

We have gone very far from the coarse suspension of sand in water when we reach these systems in which the particles are so fine that they are invisible to the eye and pass freely through the pores of the densest filter paper. It is at this point that controversy begins to be possible as to whether we are dealing with suspensions, that is, systems composed of more than one phase, or with homogeneous solutions in which only one phase is present. In other words, we are now dealing with a typical colloidal solution of a metal.

Before discussing the properties of these liquids we will consider the effect of beginning at the other end of the scale, and examine in what manner somewhat similar systems may be obtained. We will begin with the homogeneous solution of salt in water, and make a gradual imaginary increase in the molecular weight of the dissolved substance. In salt solution itself the salt is probably present as single molecules of sodium chloride which are bound in some way to a certain number of water molecules. Almost the only analogy which such solutions display to the suspensions we have been considering

is to be found in a curious observation made by Lobry de Bruyn and van Calcar, who investigated the behaviour of sodium sulphate solutions under the action of powerful centrifugal force. They found that, on being rapidly whirled, a strong solution crystallised out at the circumference. This resembles the sedimentation of clay suspensions under the action of gravity, except that a more intense force is required to cause the separation.

More striking phenomena of a different kind have been observed with substances of a greater molecular weight, such as sugar. It has been shown by Spring that aqueous solutions exhibit the Tyndall effect, which is the phenomenon observed when a ray of light is passed through a long tube filled with the liquid in question. If the liquid is not what is termed "optically pure," on looking sideways at the tube a shimmering can be seen which recalls the appearance of a ray of sunlight shining into a dusty atmosphere. The cause of this shimmering is the polarisation of the light by the minute suspended particles. With gases Tyndall found that it was very difficult to remove all suspended dust particles ; indeed, the method finally adopted was that of coating the floor of the tube with a layer of glycerine and allowing it to stand for some time. In this way the dust particles were fixed by the glycerine, leaving the gas in the tube optically pure, so that the path of a beam of light could no longer be traced when the tube was examined from the side. Spring experienced similar difficulty in obtaining solutions of salts which were optically empty. In the case of salts of the alkali metals he succeeded in doing so by an ingenious method somewhat similar to that by which an optically pure gas was obtained. The solution was placed in the tube and a gelatinous precipitate such as ferric hydroxide was formed there by the addition of suitable reagents. As the precipitate settled it carried down the particles of dust, leaving a solution which was practically optically pure. The method was not successful with solutions of the salts of aluminium, zinc and other metals. The residual effect is explained by the presence of the hydroxides of these metals, formed by hydrolysis of the salts. In the case of sugar solutions also it was not possible to attain complete

optical purity: the faint shimmering which remained, after careful optical purification on the lines indicated, points to the presence of minute particles polarising the light. The solution was not absolutely homogeneous, and as the formation of insoluble compounds is not possible here, this can only be ascribed to the action of the sugar molecules. It is very likely that they may be associated with a number of water molecules, but nevertheless this visibility of the molecules is very remarkable, especially for a compound such as sugar, which can crystallise perfectly, and which yields normal values for the molecular weight by the freezing-point and boiling-point methods. Indeed, sugar will diffuse through a parchment membrane and is a typical member of the crystalloid class. It must be noted, however, that the existence of the Tyndall effect does not show that the molecules are actually visible to the eye, since particles which are so small as to lie far beyond the limits of visibility by the eye can exert a polarising action on a ray of light.

With more complex organic substances, such as the proteins, which possess very high molecular weights, an opalescence of the solutions can be observed even with the naked eye. This is probably an enhanced Tyndall effect. Here, however, much more striking properties are shown. The solutions, of which egg-white may be taken as an example, do not crystallise except occasionally with the greatest difficulty, and have lost the crystalloidal property of diffusing through a parchment membrane. In short, we have now to deal again with a colloidal solution.

It is thus possible to arrive at the colloidal state by a series of transitions, none of which need be very sharp. Although only one or two of the midway states have been given, the gradation is very complete in Nature. We have started from either a true solution of an electrolyte, or from a coarse suspension of a solid in a liquid. In the borderland lie the class of colloids.

When we consider that many substances occur in both the colloidal and crystalloidal states, the view which appears most plausible is that the colloidal state is merely one of the states which can be assumed by any kind of matter. In precisely the

same way we can regard the crystalloidal state as one which can also be assumed by any kind of matter. In each case it happens that to the present we are not familiar with both states for many substances. Thus hitherto rubber has not been obtained in the crystalloidal state. At the same time the number of substances known in both states is rapidly increasing; most of the elements and many compounds are known in both states. A good analogy for this mode of regarding the colloidal state is given by Wo. Ostwald, who remarks that in thermochemistry we do not speak of two classes of bodies, hot and cold, but that we consider all bodies in a hot or cold state; both states can be assumed by the same body.

Following Wo. Ostwald, Colloidal Chemistry may be defined as that branch of chemistry which treats of the properties of matter in the colloidal state. Accordingly it is now necessary to discuss the especial properties which distinguish matter in this state.

In harmony with the observation already made, that colloids occupy an intermediate position between suspensions and true solutions, the view which appears most worthy of acceptance is that which considers the essential characteristic of colloidal solutions as lying in their heterogeneous nature (*i.e.*, difference between neighbouring parts of the solution). In this way they are regarded as systems in which more than one phase is present. Simple as it appears, this view has only been reached after much controversy, and the question can perhaps scarcely be considered as finally decided even yet. It would require too much space to give any detailed account of even the more important reasons which have led to this conclusion. It will be more fitting here to outline the manner in which this conception helps in arriving at a comprehensive picture of the phenomena, and then to describe two classes of colloids. In this way the ground will be cleared for the purpose of describing rubber itself, which has been styled "the colloid *par excellence*."

Colloidal solutions then are composed of a liquid—in rarer cases a solid or a gas—which contains distributed throughout itself another phase. This phase may be either solid, liquid or gaseous. Foam is an example of a gas distributed throughout

a liquid. When a solid is distributed throughout a liquid the system is analogous to a suspension, while where another liquid is concerned there is a resemblance to an emulsion such as milk. An emulsion is merely a suspension in which the particles are liquid.

We may leave out of consideration the case in which gases are concerned. Before classifying the others it may be noted that the liquid or solid in which the other phase is distributed is termed the "continuous phase" or the "dispersion-medium." The phase which is distributed or dispersed throughout the continuous phase is termed the "disperse phase." Thus in a clay suspension, clay is the disperse phase and water is the continuous phase or dispersion-medium. In rubber latex or in milk, the globules of rubber or of fat are the disperse phase, while the aqueous liquid, or serum as this is termed, is the continuous phase.

It has been said that the degree of fineness of the disperse phase has much to do with the properties of the system. This is termed the "degree of dispersion." A system in which the disperse phase is present in a very fine state of division is one of high dispersion; a coarser-grained structure corresponds to a low degree of dispersion. Thus fine sand in water has a higher degree of dispersion than fine shot, but a lower degree of dispersion than a colloidal solution of a metal such as can be prepared by the methods of Bredig or Svedberg. Degree of dispersion is a measure of the "fineness of grain" of the system.

Suspensions and emulsions are thus systems of low degree of dispersion, and differ from colloidal solutions which show a high degree of dispersion. The difference is essentially one of size of particles. Apart from this, it has been shown above that there are resemblances; colloidal solutions are actually classified according to their similarity to either suspensions or emulsions. When the disperse phase is solid the colloid is termed a "suspensoid," while when the disperse phase is a liquid it is termed an "emulsoid." In this connection it must be remembered that the modern conception of a liquid is a very wide one. Matter is considered as being divided into the classes of solids and fluids: the latter class including liquids and gases. The essential

characteristic of the solid state is regarded as lying in the ability to crystallise, and thus all bodies which cannot be regarded as crystalline are strictly to be considered as fluid. In this way all ordinary liquids and gases are "fluid," and also many substances which would at first appear to be solid, such as the so-called amorphous substances. It has been shown that many of these are really microcrystalline, but the remainder are classed as liquid. The explanation of the classification is that they are really highly supercooled liquids, such as glass. Again, substances such as pitch are merely liquids of very high viscosity.

Among the emulsoid colloids, possessing a liquid disperse phase, are comprised the proteins, the nitrogenous substances which occur so widely in the animal and vegetable kingdoms, and, indeed, most of the organic colloids including, of course, rubber. In fact, most of the colloidal substances of physiological and industrial importance belong to the emulsoid class. It is unfortunate for the technologist that the colloidal chemistry of these substances is still extremely obscure. Wo. Ostwald mentions among the colloidal industries the following:—Dyeing, tanning, soap, rubber, sewage purification, photography, lubrication, starch, brewing, clay and cement, etc. Except in the last instance the fundamental substances are all organic, though in the case of photography an inorganic substance is intimately concerned.

The suspensoid colloids, in which the disperse phase is solid, are, on the contrary, as Freundlich observes, nearly all laboratory products. Among them are to be found the colloidal solutions of the metals, and many other inorganic colloids. Since in this class the phenomena are comparatively much simpler, we will now consider a typical suspensoid, colloidal gold, and incidentally colloidal metals in general.

It has long been known that when a piece of phosphorus is placed in a solution of gold chloride a most beautiful red liquid is obtained. A similar result can be attained by the use of other reducing agents such as ferrous sulphate. The question was raised as to whether this deep red liquid was to be regarded as a solution of gold in the metallic or other state, or whether it rather consisted of excessively fine particles of gold suspended in

the aqueous liquid. On the one hand, the liquid appeared quite homogeneous to the eye and passed through the pores of the finest filter paper. On the other hand, Faraday pointed out that if the liquid was examined with a lens in sunlight, particles seemed to be visible. At the same time, it was difficult to explain the superb colour. Later investigators have obtained similar solutions by reduction of gold salts with oxalic acid or formaldehyde. When placed within a parchment membrane surrounded by pure water, the electrolytes diffuse out, leaving the gold suspended in a dispersion-medium which is practically pure water. The process of purification is termed dialysis. These solutions display the Tyndall effect to a marked extent, as would be expected from the behaviour when examined in sunlight with a lens. It was an elaboration of this effect which led Siedentopf and Zsigmondy to the discovery of the ultramicroscope in 1903, making an advance in the methods of colloidal chemical research the importance of which is immense, since the possibilities are so vast.

By the aid of the ultramicroscope it is possible to examine the Tyndall effect under the microscope. The solution which is being examined is placed in a small quartz cell at the focus of the microscope. A powerful beam of light is directed laterally into the liquid. It is important to secure a dark background so that no light can enter the eye direct. Under these conditions the light is scattered and polarised by the particles, which are thus rendered visible as luminous points. Though the particles are smaller than half a wave-length of light, yet they can still become visible in this way by the effect which they exert on the light.

When a solution of colloidal gold of moderate degree of dispersion is examined, the single particles can thus be observed. If the degree of dispersion is very high, the particles are no longer seen individually, but the field of vision appears to shimmer: only a general illumination results. In this way it is possible to measure the degree of dispersion by diluting the liquid till the particles are few enough to count, according to the method used in counting the corpuscles in blood. Knowing the number of particles in a given area of the field of the microscope, and the concentration of the solution, it is easy to calculate the size,

assuming that the particles are spherical. The diameter is expressed in millionths of a millimetre. It must be remembered that a tenfold increase in diameter corresponds to a thousand-fold increase in volume and consequently in weight.

Taking as unit the one-millionth part of a millimetre,[1] the smallest particle that can be seen with the microscope is one of approximate diameter 100. This diameter represents the lower limit of microscopic vision. The smallest particle which can be detected ultramicroscopically has a diameter of about 1 unit. For the sake of comparison it may be added that the wave-length of sodium light is about 590 units, while the diameter of a molecule of hydrogen is about one-sixth of a unit. According to Zsigmondy the region of colloidal solutions extends from particles of diameter 100 to those of diameter 1. If the disperse phase is larger in diameter than 100 units,[2] in which case the particles should be visible microscopically, the system is a suspension or an emulsion. If the diameter of the particles is less than 1 unit,[2] when the particles are no longer visible even with the ultra-microscope, the system is a true solution, and is considered to be homogeneous. The limits for colloidal solutions do not appear wide till it is recalled that a difference in diameter ranging from 1 to 100 units means a difference in weight from 1 to 1,000,000.

The limits are not strictly defined. Thus the colloidal solution of arsenic sulphide prepared by Picton contained particles which were visible in the microscope; those of antimony sulphide could not be seen in this way.

The solutions which possess colloidal properties are termed "sols"; a prefix is used to denote the nature of the continuous phase. Those in which the medium is water are the "hydrosols," whilst the "organosols" are those in which the medium is an organic liquid. If this is alcohol they are termed "alcohosols," and so on. Under certain conditions the colloid can separate out in an amorphous form which is termed a "gel"—"hydrogel" if it has resulted from a hydrosol.

It has already been mentioned that gold hydrosols can be prepared either by reduction of gold salts or by electrical

[1] A "micron" is equal to 1,000 of these units.

[2] It must be remembered that these values are only approximate.

pulverisation of metallic gold. These hydrosols have been obtained, especially by Zsigmondy, in various forms whose colour is rose, red, violet or blue. The size of the particles, or the degree of dispersion, can be made to vary enormously, so that all gradations may be observed between a suspension, where the diameter is about 1,000 to 3,000 units, and a solution where the particles are so small that the liquid is practically optically empty. In the former state the particles are so coarse that they can be seen by the eye as a turbidity.

The behaviour of gold and other hydrosols on filtration is instructive. Through paper filters filtration is practically impossible as a means of separation, since the particles are smaller than the pores of the paper. The solution simply "runs through"—a colloidal phenomenon which frequently causes much trouble in ordinary analysis. The usual methods for preventing this depend on increasing the size of the particles, *i.e.*, diminishing the degree of dispersion, usually by the addition of electrolytes, as will be described later.

In the cases we are considering this difficulty can be overcome by the employment of special filters. Examples of such "ultra-filtration" have been studied by Bechhold, who used filter paper which have been impregnated with jellies of various concentrations. Thus by using paper which had been soaked in gelatine solutions, filters were obtained which freely permitted the passage of water and crystalloid substances dissolved in it, but which retained the disperse phase of metal and other hydrosols. The pores of the ultra-filters prepared from dilute solutions of gelatine were smaller than when stronger solutions had been used, so that a series of ultra-filters could be made of increasing size of pores. In this way it was possible to arrive at an estimate of the degree of dispersion of a colloid by determining which of the ultra-filters was impervious to the disperse phase.

In the case of suspensions, Schneider and Barus estimated the size of the particles by measuring the velocity with which the disperse phase settled out under the action of gravity. Naturally this method cannot be applied to colloidal solutions, since they are comparatively quite stable as far as gravity is concerned. It is known that the velocity of sedimentation of

suspensions can be accelerated by the application of centrifugal force, and it is actually found that in this way metal hydrosols deposit the disperse phase in the form of a fine dust. The method is employed in rubber analysis to hasten the separation of excessively fine particles. When vulcanised rubber containing mineral matter is dissolved in various solvents it is frequently impossible to filter the solutions, owing to the fineness of the particles. Again, in the examination of raw rubber, the insoluble matter is often extremely difficult to separate. The difficulty is enhanced by the viscosity of the solutions, which also hinders settling. In these cases centrifugal force can be of use in effecting a separation.

The particles of colloidal solutions exhibit some very curious movements, both under normal conditions and when submitted to the influence of a powerful electric field. In ordinary circumstances all particles of less than a certain size display continuous movement, which is named the "Brownian movement" after its discoverer, Brown. It may be observed in suspensions or emulsions if the particles are not too large. When rubber latex is examined under an ordinary microscope, the rubber globules are seen to be in a state of continual oscillation. The movement is much more pronounced in the smaller globules where it appears as a zigzag motion of irregular character. The same movement can be observed in colloidal solutions under the ultramicroscope: Schidrowitz has noted its occurrence in rubber solutions.

The Brownian motion takes place round a centre, but a continous movement of the particles can occur when a suspension, emulsion, or colloidal solution, is subjected to the influence of an electric field. If the liquid is contained in a vessel into which two electrodes are dipped, and a high voltage is applied, the particles are often found to move in the direction of one of the electrodes. This is due to the fact that they usually possess an electric charge. In the cases of clay suspensions in water and of rubber latex the disperse phase possesses a negative charge: the corresponding positive charge is distributed throughout the continuous phase. Consequently in an electric field the particles wander towards the positive electrode. This phenomenon is

called "electrical kataphoresis," signifying "a wandering." It is observed in most hydrosols, which usually possess a negative charge. When the disperse phase is of a basic nature, such as colloidal ferric hydroxide, the charge is positive and the particles wander towards the negative electrode.

The particles which have lost their charge are precipitated out at the electrode. This naturally raises the whole question of the precipitation of colloids. The general phenomenon is termed "coagulation"; it consists in the change from the hydrosol into the hydrogel form. It is accompanied by a diminution in the degree of dispersion. This may be observed on a large scale in the coagulation of rubber latex, when the single globules coalesce to a mass of rubber; though the term "coagulation" is perhaps not strictly applicable here; some writers have proposed to replace it by "coalisation." A more typical example of coagulation is that which occurs when an electrolyte is added to a gold hydrosol, causing the metal to separate in the form of shining flakes: here clearly the degree of dispersion is lowered. This process of coagulation is a very general and important one, and some writers have compared it to the crystallisation of a crystalloid. We may consider the means by which it can be effected.

It has been long known that extremely fine suspensions of clay in water, which could be kept unchanged for months, might be caused to settle out quite rapidly by the addition of electrolytes. Elaborate researches have been carried out by Hardy and others with hydrosols on these lines, and certain very striking regularities have been discovered. Schulze worked with arsenic sulphide hydrosol, which was prepared by the action of sulphuretted hydrogen on solutions of arsenic trioxide containing no electrolyte. To investigate the coagulation of the hydrosol, which is a faintly turbid yellow liquid, a drop was added to a given volume of solutions of various salts, at different concentrations. No change occurred with very dilute solutions of the salts, but at a certain concentration, which was quite definite for each salt, coagulation was indicated by the formation of a yellow precipitate of arsenic sulphide. The effect was found to be practically independent of the nature of the negative ion (*i.e.*, the acid portion which is electrolytically dissociated in solution) of the salt, since

different salts of the same metal showed very similar results. Enormous differences were observed when the positive ion (the metal of the salt) was changed by taking different salts of the same acid. The chief factor proved to be the valency of the metal. Thus the coagulative power of salts of the same acid with a monovalent, divalent, and trivalent metal was found to be in the ratio 1 : 20 : 350; *e.g.*, the coagulative power of aluminium sulphate is approximately 350 times that of sodium sulphate. On account of this high coagulative power of aluminium salts, alum has been used in the coagulation of rubber latex, which takes place according to similar laws. This question will be discussed more fully later.

It has been mentioned that the particles of most colloidal solutions are electrically charged. It is a general rule that, when the disperse phase is negatively charged, it is the positive metal ion of an electrolyte which has the preponderating effect in determining coagulation. Thus arsenic sulphide hydrosol and the hydrosols of the metals are chiefly affected by salts whose metal ion has a high valency. The hydrosols of a basic character, such as ferric hydroxide, are chiefly affected by salts in which the acid ion has a high valency.

With a given salt the coagulation can only be effected above a certain concentration. As it is the ions of the salt which are active, it is evident that the more highly dissociated the solution the greater will be the coagulative action. Thus the strong acids are more powerful than the weak ones.

In harmony with the view that coagulation is connected with neutralisation of the charge of the particles, it is found that coagulation can be effected by the direct action of an electric field, as was mentioned in discussing kataphoresis. An instructive experiment is given by Hardy, who took a protein solution which was chemically neutral. It was found that the particles did not wander in an electric field. On the addition of a trace of acid they wandered towards the negative electrode, showing that they were positively charged. The direction of movement was reversed by the addition of a trace of alkali in excess : the particles were then negatively charged. This is to be explained by the property possessed by the proteins of behaving both as a base

and as an acid, by virtue of the $-COOH$ and $-NH_2$ groups which they contain. On the addition of acid the basic character of the molecule comes into play so that the particles become positively charged. When alkali is in excess the protein acts as an acid, when the charge becomes negative. Experiments such as these were so suggestive that Hardy was led to the conclusion that the stability of a colloid depended on the presence of an electric charge, and that when this charge was neutralised the system could no longer exist in the same form, but that coagulation set in, thereby lowering the degree of dispersion. This conclusion, that coagulation essentially consists of electrical discharge of the particles, does not now appear to be so generally true as was thought at the time. Nevertheless it may be stated that usually coagulation is effected by the addition to the solution of ions or other particles of opposite charge to that possessed by the disperse phase of the colloid. It is an interesting fact that colloids which are oppositely charged can exert this action. The positive ferric hydroxide hydrosol can form a precipitate with the negative gold hydrosol under certain conditions of concentration. This line of explanation has been applied with some success to the question of the precipitation of proteins by the alkaloid reagents, such as phosphomolybdic acid, which are of colloidal nature. The great activity of aluminium and iron salts in coagulating negative hydrosols is probably to be explained, at least partially, by the presence, in the solutions of these salts, of positively charged particles of the hydroxides, produced by hydrolysis.

$$FeCl_3 + 3\ H_2O \rightleftharpoons Fe\ (OH)_3 + 3\ HCl.$$

This is borne out by the fact that Spring found it impossible to prepare solutions of these salts which were optically empty.

An opposite effect can be produced by adding to one colloid another which has the same kind of charge but which is more stable towards coagulative influences. Thus Müller quotes the gold sol prepared by Zsigmondy, which was so sensitive to electrolytes that ½ cub. centimetre of 10 per cent. sodium chloride solution was sufficient to cause a colour change from red to blue in 5—10 cub. centimetres of the sol. The colour change

indicated in this case a change in degree of dispersion. If a small amount of a solution of glue, gelatine or other organic colloids is added to the sol, this is rendered so stable that even large additions of sodium chloride do not cause coagulation. The gelatine is said to exert a "protective action," and colloids which behave in this way are termed "protective colloids." The protective colloid is assumed to surround the other colloid, and the particle thus formed has a stability greater than that of the colloid which is protected, provided that the protective colloid itself is more stable. The same effect is observed in emulsions; as will be shown latter, it plays an important part in the preparation of rubber from the latex. The protective action of gelatine can be readily shown by adding barium chloride to a solution of a sulphate which contains gelatine, when the formation of a precipitate of barium sulphate can be entirely prevented. Similar actions lie at the root of many of the cautions given to remove organic matter at various stages of inorganic analysis. Zsigmondy measures the strength of this protective action by a number which he calls the "gold number." This is equal to the weight in milligrammes of the colloid which is sufficient to stop the colour change in 10 cub. centimetres of his gold sol when 1 cub. centimetre of salt solution is added.

Metal sols possess a remarkable property, by virtue of which they were described by Bredig as "inorganic ferments." When added to solutions of hydrogen peroxide they exert a marked acceleration of the velocity of decomposition, even when present in very small amount. The sols can be poisoned by carbon bisulphide or hydrocyanic acid, which causes them to lose their activity.

Summing up the properties of the suspensoids, it may be said that in general they are those which might be expected in systems consisting of a highly dispersed solid phase, usually inorganic, suspended in a liquid dispersion-medium.

In the case of the emulsoid colloids, where a liquid disperse phase is distributed throughout a liquid dispersion-medium, the properties are often more unexpected. The most complex phenomena occur, and it is frequently difficult to explain

the experimental facts, or indeed in many cases to reconcile apparently contradictory data. This is all the more unfortunate, in that the substance with which we have to deal, rubber, belongs to this class, like most other technically important organic substances.

It must be repeated at the outset that when we speak of a liquid disperse phase we do not necessarily mean a liquid in the ordinary sense of the word. We rather imply what used to be meant by the term "amorphous"—a body which is non-crystalline. Bearing this in mind, it will be understood that rubber, starch, glue, the fibres which receive the dye in various dyeing operations, gelatine, the proteins and many other organic substances fall into the class of liquids, in the strict meaning of the word. These bodies represent the gel modification of the colloids in most cases. It is first advisable to consider the hydrosols which correspond to these gels.

Such colloidal solutions frequently exhibit opalescence or show a different colour by reflected and transmitted light. When they are examined ultramicroscopically it is often impossible to detect the presence of single particles, as a mere general illumination of the microscopic field is seen. Wo. Ostwald gives the case of gelatine solutions, in which Zsigmondy observed illuminated specks when the solutions were strong: on diluting the solution these luminous points decreased in number and brightness. This is explicable when it is remembered that the system is one of two liquid phases which can dissolve in one another. The disperse phase is composed of gelatine containing a little water; the continuous phase, of water with a little gelatine. As the solution becomes more dilute the two phases approximate in their properties. Now, the visibility of a particle depends on the difference between its index of refraction and that of the surrounding liquid. The familiar example of a glass rod dipped in glycerol may be recalled, where the rod is almost invisible because its index of refraction is very slightly different from that of glycerol. In the same way, as the indices of refraction of the disperse and continuous phases become more and more nearly equal, it becomes increasingly difficult to detect the heterogeneous nature of the liquid by optical methods. This holds for the

emulsoids in general. Dealing with two liquid phases the indices of refraction are not so widely different as in the case of the suspensoids, where one phase is solid. Thus it is usually more difficult to detect the particles with the ultramicroscope in emulsoids. Despite this, particles have been detected in rubber, even in the gel form, *i.e.*, in the ordinary apparently solid rubber.

As it is not always possible to measure the degree of dispersion ultramicroscopically for this reason, other methods suggest themselves, in particular the behaviour on filtration. Like the suspensoids, these solutions often pass through the pores of paper filters, but can be retained by the ultra-filters made by soaking paper in jellies, themselves emulsoid, of various concentrations. However, as will be seen with rubber, the velocity of filtration, even through paper filters, may be very slow, though this is connected with the high viscosity of the solutions and the clogging of the pores of the filter by the suspended impurities.

The question of the molecular weight of emulsoids has been much discussed, but it appears that they can exert a very slight influence on the boiling-point and freezing-point of the continuous phase. This leads to the assumption of an extremely high molecular weight. The effect is so small that it has been considered that it may be due to the impurities accompanying the colloid, and that if these could be completely removed the effect would vanish. The results, however, lend some support to the view that in the proteins, at all events, we are approaching the state of colloidal solution rather from the side of the molecule than from that of the particle in suspension. The two modes of consideration really shade into each other, but we may perhaps regard colloidal protein solutions as containing very large molecules rather than very small particles. Still, from what has been said above, it will be seen that probably the distinction is more imaginary than real.

A marked difference between emulsoids and other colloids is the high value which is often found for the viscosity. The viscosity of suspensoids is usually not very different from that of the pure dispersion-medium, but the addition of an emulsoid may

raise the viscosity to a value hundreds of times that of the dispersion-medium. Even very small concentrations of gelatine are sufficient to raise the viscosity of water enormously: the effect increases rapidly as the concentration of the gelatine rises; temperature has also great influence. This can be observed to a less extent with rubber solutions.

Another difference lies in the fact that emulsoids do not usually exhibit the phenomenon of wandering in an electric field, as the suspensoids often do. In fact the whole question of the coagulation of emulsoids does not appear to be connected nearly so intimately with the charge on the particle as was the case for the suspensoids. Indeed, perhaps the chief difference between the two classes of colloids is their behaviour to coagulative agencies. The suspensoids, such as gold hydrosol, are coagulated by the addition of minute quantities of electrolytes. The coagulated gold is not again soluble in the medium (water) unless protective colloids are present. The coagulation is irreversible. This is so far from being the case with protein solutions that coagulation with salts, which is termed "salting-out," is employed as a method for the isolation of the proteins, since it leaves the colloid almost unchanged. Further, the amount of electrolyte required is very different. The concentration required to salt out a protein is quite high: the salt must be added till the solution is about normal, though the amount varies. In this way the protective action of emulsoids is explicable, since the protective layer coating the suspensoid particles will be unaffected by the concentrations of electrolyte which are capable of coagulating the pure suspensoid.

It has been said that the coagulation of emulsoids by salts is reversible, since the precipitate is again soluble in the dispersion-medium. The emulsoids can be coagulated by other means, such as boiling, when the precipitated colloid is not again soluble.

All emulsoids are not organic. Thus various hydroxides, such as those of aluminium and iron, belong to this class. These sols may be obtained by dialysis of solutions of the chlorides of the metals. Ferric hydroxide hydrosol is a deep reddish brown liquid; the particles are positively charged. Ordinary ferric chloride solutions contain a certain amount of the hydrosol,

formed by the hydrolysis of the salt by water. Another inorganic emulsoid is the hydrosol of silicic acid, obtained by dialysis of sodium silicate solutions. It is obtained in the hydrogel form as a gelatinous precipitate, on treating the same salt with hydrochloric acid. Incidentally it may be noted that the well-known difficulty experienced in washing gelatinous precipitates is due to their colloidal nature, which causes them to retain the last traces of dissolved salts with great tenacity.

The removal of the last traces of water from a colloid in the gel form is attended with similar difficulty. In both cases the cause of the retention is the adsorption of the moisture or dissolved substance by the colloid. Adsorption is one of the general phenomena exhibited by colloids, which will receive particular mention in the chapter on vulcanisation.

Under many circumstances the emulsoids can be obtained in an apparently solid form, such as glue or rubber. The structure is to be considered as of a honeycomb nature, so that the surface is really very great. Hence the substance may be imagined as possessing a degree of dispersion which is very considerable compared to that of ordinary solids.

A remarkable property of matter in the gel form is that of "swelling" in various solvents. When it is brought into certain dispersion-media it absorbs large quantities of these liquids, giving an apparently homogeneous mass, which in reality consists of a very concentrated emulsoid colloidal solution. The process is a continuous one to which there is no sudden limit such as that found in the saturation-point of solutions of crystalloids. For this reason it is often said that it is incorrect to speak of the "solution" of such gels in liquids, *e.g.*, of rubber in benzene. Yet the term colloidal "solution" can be legitimately used. At all events, the term is convenient and will be employed in the analytical part of this work, where the "swelling" of rubber will be further discussed.

It is hoped that enough has been said now on the general subject of colloids to serve as a groundwork, on the basis of which future references and explanations can be made in due course. It is well to lay final emphasis on the modern view that colloids and crystalloids are not different classes of substances, but merely

different and, indeed, complementary states which may be assumed by all kinds of matter eventually. Nevertheless, up to the present, rubber has only been known in the colloidal state, though gutta-percha is stated to have been obtained crystalline.

THE LITERATURE OF COLLOIDS.

"Grundriss der Kolloide," by Wo. Ostwald, has been especially consulted in the compilation of this section, in addition to the "Kapillar-Chemie" of Freundlich. Shorter works, which may be recommended to those who wish to pursue the subject further than this short sketch, are "The Colloidal and Crystalloidal State of Matter," by P. Rohland (translated by Britland and Potts), and "An Introduction to the Chemistry of Colloids," by V. Poschl (translated by Hodgson). The former deals at greater length with the applications of colloids in science and technology, while the latter considers more fully the properties of the suspensoids. The "Zeitschrift für Chemie und Industrie der Kolloide" is a monthly journal devoted to olloids.

CHAPTER II

RAW RUBBER

In the preparation of raw rubber it is usually necessary to secure the latex by tapping the tree. The latex is then coagulated by various methods. The resulting rubber is washed with water between rollers, and dried, either at the place of preparation or at the factory of the consumer. The product is the material known as "technically pure" rubber, which is ready for use in manufacture.

As far as the tree itself is concerned, the possible choice is large. Some of the more important rubber-yielding trees and plants are:—Hevea Brasiliensis, Castilloa Elastica, Ficus Elastica, Funtumia Elastica (Kickxia), Manihot Glaziovii, various vines of the genus Landolphia, and the herbaceous plant Parthenium Argentatum. They are all tropical or sub-tropical.

The principal of these trees is, of course, the Hevea, which furnishes the standard grade, Para rubber. Formerly the only source was the forests of the Amazon valley, but within the last few years the planting industry in the East has made enormous strides, which have resulted in an output of cultivated rubber, large at present, which will be enormous in the near future.

A discussion of planting problems as such would be out of place here. For our purpose we may assume that the problem of securing a sufficient number of healthy trees, either wild or plantation, has been satisfactorily solved.[1] We may further assume that the best method of tapping has been devised to yield the maximum of latex with the least injury to the tree. So far, these are questions rather concerning the botanist and mycologist than the chemist, though a very interesting phenomenon may be mentioned, that of wound response, which appears intimately

[1] Wright, "Hevea Brasiliensis"; Wicherley, "The Whole Art of Rubber Growing," may be consulted.

connected with the osmotic pressure of salts in the tree-juices. It is found that when the Hevea and certain other trees are tapped daily, the yield of latex increases up to a certain point; the early tappings have a stimulating action.

Once the latex has been obtained, a complex chemical problem is involved in selecting the most suitable method of coagulation and subsequent treatment, in order to secure rubber of the best quality which will be as uniform in its properties as possible. This latter point cannot be said to be solved yet, though the emphasis which has been laid upon it from the standpoint of the manufacturer, in the technical press and at the recent exhibition, should focus attention upon it more closely.

There is involved here a colloidal system : rubber latex essentially consists of an emulsion of liquid rubber in water; other substances are also present, particularly protein, resin, sugars, and small quantities of salts. The rôle of the protein is a very important one, since it appears to act as a protective colloid, preventing the coalescence of the rubber globules. The process of coagulation thus depends on the destruction of this protection, and an examination of the methods which are used will reveal this principle at the root of them all.

The function of the rubber itself in the plant is still obscure; the researches of Harries appear to indicate that it may serve as a reserve foodstuff to be drawn on in time of need by the plant. This view was put forward before, but the work of Harries has confirmed it by leading to the suggestion that the plant may be able to break down the rubber to sugars. At present this must be regarded as unproved. Others have considered that the rubber fulfils the object of protecting the tree against wounds, as a coating of rubber results from the coagulation of the latex exuding from the incision. It scarcely seems probable that such immense quantities would be secreted for such a purpose.

In considering the function of the protein we are on securer ground. Not only are proteins normal constituents of plant juices, but in the present case they maintain the rubber globules in a state of emulsification. Chemically, they are complex nitrogenous bodies formed, probably in the sieve-tubes, from the carbo-

hydrates of the plant by combination with oxygen-nitrogen compounds. From the results of estimations of the nitrogen-content of various proteins, the percentage of nitrogen in rubber proteins is taken as 16, so that 1 per cent. $N = 6{\cdot}25$ per cent. protein present. The proteins are bodies which can act both in a basic and acidic capacity, owing to the—NH_2 and—$COOH$ groups which they contain. As emulsoid colloids, their stability against coagulative influences is considerable, as compared with suspensoids or with simple emulsions.

The resins may be considered as by-products of the manufacture of rubber by the plant. In composition they are distantly related to rubber itself. As invariable constituents of raw rubber they will require detailed discussion later.

The sugars and salts are more usual constituents of plant juices.

The process of coagulation (or, as it might be more correctly termed, coalisation, since the essential feature is the coalescence of the rubber globules) is one apparently depending on the removal of the protective film of protein or other protective colloid. The globules rise through the liquid, coalesce, and yield a tough elastic mass of rubber, which may be regarded as an emulsoid gel. Coagulation is evidently a colloidal problem. Yet the actual coagulation is a relatively simple matter till the quality of the resulting rubber gel is considered. Much depends on the completeness, and therefore to some extent on the speed, with which the liquid rubber in the globules changes to the tough elastic gel. Incomplete coagulation will tend to make the rubber "tacky" (see later), while, as Schidrowitz has pointed out, coagulation with an excess of acetic acid is liable to lead to a very close-meshed and consequently brittle rubber. Further, the colour at all events seems intimately connected with the presence of degradation products of the proteins, probably of a phenolic nature. This again depends on the presence of ferments in the latex, which are capable of accelerating decomposition.

In studying the processes of coagulation, it is advisable to begin with an account of the method by which Hevea latex is coagulated on the Amazon (yielding fine hard Para rubber), on account of its historical and commercial importance.

The trees, which are found in the hot, damp valley of the Amazon, are tapped in the dry season. The collector selects a tree of about 2 feet in girth and makes a series of incisions in the bark. Receptacles are fastened under each cut, and after a few hours, when the flow of latex has ceased, the contents of these cups are transferred to a larger vessel. Coagulation is effected by smoking the latex over a wood fire on which palm nuts (Urikuri) are burning. A paddle is dipped in the latex and rotated in the smoke. After some time more latex is poured on, and the process is continued till a mass of rubber of considerable size is obtained. After removing the paddle by cutting the lump in half, the rubber loaf is ready for shipment.

In this extraordinary process the coagulation is effected by the combined action of heat and smoke. These nuts in burning give off carbon dioxide, acetic acid, creosote and other substances. The rubber is deposited in successive thin films, each of which is thoroughly exposed to the action of the smoke, so that coagulation is complete. Further, the sterilising action of the smoke on the ferments present tends to inhibit the decomposition of the protein. In spite of the apparently crude nature of the process, it yields rubber which is, on the whole, better than any other. It has not yet been definitely decided whether this is due to the great age of the trees at the disposal of the worker in the Amazon valley, to the actual method of coagulation, or to a possible difference between wild and cultivated trees, either because the latter may not be descended from a stock representing the best Amazon trees, or because of a difference in growth of the tree away from its natural home. Concerning the last point, Berkhout has given the very instructive analogy of quinine, which is obtained from the cinchona tree, originally indigenous to Peru. The tree was planted in Asia, and in a few years the quinine from Peru was driven out of the market. It has not even been satisfactorily demonstrated that fine hard Para is superior to the best plantation rubber, though the slightest experience of rubber mixing is sufficient to show that the latter is practically always softer on the rolls in mixing. This indicates a difference, though the exact significance of this difference from the point of view of quality is not easy to elucidate. It

will be mentioned later that chemically the rubbers are very similar.

The most striking features about fine hard Para are its almost invariable good condition, its uniformity (a quality of fundamental importance), and its excellent "nerve." "Nerve" is a term which is very useful, but difficult to define. Speaking generally, it connotes high elasticity and good wearing properties.

Before discussing the theory of the processes employed on the plantations, the following classification of methods of coagulation may be quoted[1]:—

I. *Coagulation by Heat.*

1. By artificial heat.
(*a*) Smoking (Amazon, Brazil and New Caledonia).
(*b*) Boiling method (Mexico, and W. Africa for latices of Funtumia Elastica).
2. By natural heat.
(*a*) Separation of the rubber in holes in the earth by evaporation or by trickling of the liquid (Angola).
(*b*) Separation on the human body (Congo, Angola, etc.).
(*c*) Evaporation on the ground (Ceara, Angola).

II. *Coagulation by Creaming.*

(*a*) Creaming after dilution with water. Filtering, washing and pressing (Bahia, Congo).

(*b*) Creaming by mechanical means. Centrifugalisation, combined with coagulation by acids (experimentally in Ceylon).

III. *Coagulation by Chemical Agents.*

(*a*) Mineral acids and agents (Gambia, Senegal, Mozambique, Matto Grosso, Pernambuco, Maranhao).

(*b*) Organic acids and plant-extracts (Ceylon, Peru, Guatemala, Gambia, Madagascar, Upper Congo, German E. Africa, etc.).

IV. *Coagulation by Beating and Soaking.*

Chiefly for root-rubber on the Congo. The cut roots, dried in the sun, are steeped in water, like flax, and the coagulated rubber

[1] Spence, Report of 1908 Rubber Exhibition.

beaten out of the rotted roots with flails (Landolphia and other root rubbers in W. Africa and German E. Africa, Guayule in Mexico).

V. *Coagulation by Chemical Treatment with Subsequent Extraction with Solvents* (Guayule in Mexico).

* * * * *

It has been shown that the quality of the rubber produced from a given latex varies greatly according to the method of coagulation employed. A particularly striking example has been given by Marckwald and Frank, who examined numerous samples of Kickxia latex, using various processes. The rubber obtained was vulcanised and tested mechanically. They concluded that the source of the latex was far less important than the method of coagulation.

Of the methods given in the above table three apply to the latex of Hevea Brasiliensis. The smoking process adopted for wild Para has been described. The majority of plantation rubber is also Hevea, and most of this is coagulated by acetic acid. More recently attention has been closely directed to a combination of these methods. The smoking process, in which coagulation is effected by blowing in smoke with steam or air, seems likely to be of importance. It may be noted that "smoked sheet" does not necessarily mean rubber which has been prepared in this way. It may only mean that the rubber has been superficially smoked after coagulation, which is quite a different matter.

The rubber globules in Hevea latex are from 500 to 2,000 millionths of a millimetre in diameter ; the degree of dispersion (see Chapter I) is thus not very high. It is, therefore, possible to separate the rubber by centrifugal force, when the globules, which are lighter than the liquid, rise and form a coherent mass. Here the explanation of the process is simple.

In the case of coagulation by acetic acid and other chemicals the mechanism is more complex. The general theory has been clearly stated by Fickendey as follows :—As Weber recognised, coagulation occurs in two stages : coalescence of the globules, and transformation of the cream into tough elastic rubber. The

first process is reversible. In ordinary circumstances it is prevented by the protective action of the colloids present in the latex, the proteins or peptones. Essentially, the mechanism of coagulation consists in the destruction of the protection; this can be effected by any agency capable of coagulating the protective colloid. Addition of acid has this effect, and consequently this causes separation of the rubber. As colloids can only exert their protective action when they are present in a sufficiently high concentration, it is possible to cause the latex to "cream" by dilution. Fickendey showed that if this rubber cream is then shaken up with a fresh solution of the colloid it can be partially re-emulsified. In practice the cream formed by coalescence of the globules changes into tough elastic rubber. The relationship between the two forms of rubber will be discussed later.

The strong coagulative power of acids is in harmony with the fact that the globules possess a negative charge. Indeed, the principle of kataphoresis has actually formed the subject of a patent by Cockerill, in which a current is passed through the latex, and the rubber separated as a thin film on an endless band which is the kathode—the globules move towards the positively charged electrode, lose their negative charge and so separate out.

Naturally, the coagulation of different latices is effected in various ways. Thus, the latex of Kickxia is one in which the protective colloid is a peptone. The peptones are only semi-colloids; they lie nearer to the crystalloidal state than the proteins, as they are able to diffuse through a parchment membrane. They are not coagulated by acids or by boiling. Accordingly these methods fail to yield rubber from the latex. This can be obtained by the addition of formaldehyde, which coagulates the peptone and thus causes coalescence of the globules; it has the further advantage of tending to sterilise the rubber. The same result can also be attained by dialysis, when the peptone diffuses through the membrane and thus ceases to exert its protective action. In fact, it has been shown by Marckwald and Frank that very high-class rubber is obtained from this latex, coagulated by pouring on a wooden plate, which is really a process of dialysis.

From the work of Kaye, Spence and others it seems that the discoloration frequently observed in plantation rubber is very largely due to the activity of ferment-like bodies or enzymes. These have the power of breaking down the proteins in the rubber, yielding degradation-products which appear to be of a phenolic nature, but containing several —*OH* groups. These are attacked by the oxygen of the air giving intensely coloured bodies which cause discoloration in the rubber. The action will be of a similar type to the oxidation of the polyhydric phenol, pyrogallol, which yields the well-known brown solution (obtained after using "pyro" developer). The activity of these enzymes is retarded by heat; it also depends on the acid or alkaline reaction of the liquid.

A defect exhibited by the less carefully prepared plantation rubbers, and by various wild rubbers, is that of "tackiness." This is another property easy to recognise but difficult to define accurately. It goes hand in hand with bad condition. A "tacky" rubber sticks to itself on pressing, even in the cold. The rubber is soft, and in bad cases presents the appearance of incipient liquefaction. It is occasionally associated with bad smell. On heating, the rubber may liquefy, though this is a property shown by soft rubbers, such as Guayule, when in sound condition. The term "tackiness" is perhaps applied most correctly when the condition is the result of a kind of disease. The causes may be partly bacterial: we shall see later that the treatment during drying may have some influence on it. The great cause of tackiness, according to Marckwald and Frank, is insufficient coagulation. To avoid it, they recommend that the rubber should be shipped moist, so that the contagion may not spread by the tacky parts "dissolving" the others. Fickendey has recently adduced evidence to show that tackiness is closely connected with oxidation. He suggests the addition of tannin to the latex, since the tannin will oxidise more readily than the rubber after coagulation, and will thus exert a preservative action.

A fault of many wild rubbers is their extremely dirty condition. Frequently this does not affect the quality of the washed product very seriously. In the case of first-class plantation rubber, which does not require washing as a rule, this

defect is not found. The exceptions are the cases in which the rubber is carelessly packed, so that fragments of wood require removal, and those in which the coagulating agent has not been completely removed by washing at the plantation. It has been pointed out that different acids differ in the ease with which they can be washed out, and in the effect which they are apt to exert afterwards. For electrical work, even traces of acid are undesirable. Thus the nature of the coagulant, of which many have been proposed, *e.g.*, Purub (hydrofluoric acid), etc., is by no means immaterial.

The chief drawback to the plantation product is its lack of uniformity. Technologists will not need to be reminded that while there is a fair constancy in the properties of wild Para, plantation rubber exhibits variations in general appearance, and especially in its behaviour on vulcanisation. The urgent need of uniformity, of such constancy that a ton purchased in January is the same as a ton purchased in June, is a point of importance which has been repeatedly urged, by the writer among others ; it is perhaps the chief problem before the planter.

It must be admitted that it is by no means a simple matter to secure this uniformity. It does not seem sufficient to devise a method of coagulation which is entirely suitable for a given latex, and to adhere rigidly to it. The quality of the latex on the same plantation varies, not only with the age of the tree, but also according to location. Kaye found latex collected in different areas of a large forest showed great variations in specific gravity and rubber content, and similar differences were even found between neighbouring trees. He recommends as a remedy careful grading and mixing in bulk. It certainly seems that some plan should be devised by which the method of coagulation can be adjusted according to the quality of the latex. These are problems concerning the planter rather than the manufacturer, but they are worthy of consideration in so far as they explain the existence of the differences in the plantation product.

Returning to the preparation of the rubber, the next process after coagulation, if this has been effected in the wet way, is washing the coagulated mass. It is worked between rollers and finally passed between a pair with diamond-shaped projections,

yielding sheets of "crêpe," so-called from their appearance. If smooth sheet is desired, smooth rollers are used. The product contains much water, and requires drying, which is generally done on the plantation.

At this stage the rubber comes within the province of the manufacturer. He receives plantation rubber in the washed and dried condition. Wild rubber arrives as it has been coagulated, and requires washing and drying. Para is washed by steeping in warm water till the loaves are softened. After the loaves are soft they are introduced (cut up first) between two grooved rollers revolving at unequal speeds under a stream of water. The rubber is passed through until the sheets are clean, when it is thinly sheeted between equal speed rollers, ready for drying. Among other methods the use of the Werner-Pfleiderer washer may be mentioned. The feature of this machine is the gentle but thorough mastication undergone by the rubber, which is passed between very deeply grooved rollers in a wire cage, entirely submerged in water. The rubber comes out in irregular twisted masses, which are passed through rollers and crêped.

The machine is very effective for soft dirty rubbers. These may be washed in cold water, or, as Esch has suggested, even ice-cold water (containing sodium carbonate) may be used in the case of sticky rubbers.

Drying may be done in air, or in vacuo. Both have advantages and there is a certain difference of opinion as to which is better.

In the method of air drying the washed rubber in thin sheets is suspended from beams placed across the top of special rooms. These drying rooms are maintained at a temperature depending on the kind of rubber. Ordinary or dried air may be sucked or blown through. The rooms are kept dark, as light has an accelerating action on chemical changes likely to occur, such as oxidation. On plantations, drying rooms are sometimes provided with windows of coloured glass to filter out the actinic rays.

In the method of vacuum drying, the rubber is placed in trays, heated by steam or electrically, in a vacuum stove. It is dried at the highest possible vacuum which can be attained. In this way rubber can be dried in one-and-a-half to two hours, as compared

with some days by the air-drying method. The process requires considerable care. On the one hand, it is possible to drive off the exterior moisture and not to touch that inside, if the rubber is not hot enough. Naturally heating is difficult since it cannot come about through convection, but only by radiation, or by conduction from the tray. On the other hand, overheating may very easily occur from the heat of the tray. In any case it is not recommended to carry the drying too far. It is possible that some of the inequalities in plantation rubber may be connected with the drying, since it is significant that rubber which has been overheated vulcanises at a different speed and yields a result different from normally treated rubber.

The progress of drying is controlled in the laboratory by moisture estimations. It must be remembered that rubber is a hygroscopic substance to a certain extent. If the rubber is masticated into large lumps before being stored the danger of becoming damp is avoided, though with a normally dry atmosphere it may not be serious. Before actually estimating the moisture the sheets are torn across to see whether any white specks of damp rubber can be seen. When these are no longer visible, the moisture may be estimated. Careful analytical control is very necessary, since to obtain the best results for many purposes the drying should be very thorough. In some cases residual moisture can be driven off on the rolls before mixing, and in drying Guayule this method is actually recommended if a vacuum stove is not available. The method of estimating moisture will be considered in detail in the analytical section of this chapter. It may be remarked that, as in the case of other colloids, the last traces of water may only be removable with considerable difficulty, since the water is adsorbed by the rubber. The researches of van Bemmelen on the removal of water adsorbed by other colloidal gels, such as silicic acid, show that the last traces may be retained with great tenacity.

The dried rubber is weighed, and the "loss on washing" is expressed as a percentage on the crude raw rubber. This loss, in the case of Para, usually amounts to about 16 per cent. The low-grade rubbers lose very much more: thus Assare Scrap may lose as much as 50 per cent. The loss consists of moisture, dirt

(sand, wood, etc.), and certain constituents of the latex such as sugars, etc. Tables have been given for the loss on washing[1] of various rubbers, but the figures are subject to great variations. A recent development is the sale of "semi-washed" rubbers, which have been partially washed so that the loss on washing can be guaranteed to a certain extent. The figure is, of course, of fundamental importance in costing the rubber used.

It is not proposed to describe the appearance of the various brands of raw rubber; actual handling is necessary here. Nor is it intended to give an extensive list of rubbers.[2] Among many other brands, we will merely mention the rubbers derived from the Hevea, wild Para, and plantation Para usually in the form of crêpe. The Manihot Glaziovii yields Ceara Scrap, an excellent though somewhat dirty rubber. The numerous varieties of African rubber, most of which are rather soft, show great variations. Some qualities are extensively used in ebonite work. Plantations in Africa and elsewhere grow the Manihot and the Kickxia. Castilloa yields the variety Caucho Ball. Guayule, which has acquired much importance recently, is a resinous rubber produced in Mexico from the shrub Parthenium Argentatum. An example of a highly resinous rubber, which is partially deresinified by special processes, is Malay Crêpe. This is obtained from Jelutong, a gum containing only about 10 per cent. rubber, which is derived from the latex of the Dyera Costulata.

* * * * *

The constituents of technically pure rubber may now be considered in detail. Beyond the most important, both in quantity and in significance, the rubber hydrocarbon itself, there are usually present resins, proteins, a small quantity of mineral matter, and the last traces of water. A certain amount of an oxidation product of the rubber itself is also probably present, though not nearly so much as was at one time supposed. It has been generally considered that the sugars are removed in washing, but Pickles and Whitfield have shown that this is by no means always true. Traces of the coagulant may be present

[1] Weber, "Chemistry of India Rubber," etc.

[2] See Pearson, "Crude Rubber and Compounding Ingredients."

in the case of plantation rubber, either because of insufficient washing, or because an unsuitable coagulant is used which is difficult to remove. Finally, among other products, traces of volatile matter may be present, *e.g.*, in Guayule there is an essential oil to which the characteristic pleasant celery smell is due.

We will consider first the most important constituent, rubber itself, of which the percentage varies from about 95 per cent. downwards. Much of the work on rubber has been done on material which has not been quite pure. Although Harries has stated that, contrary to the majority of colloids, rubber can be readily obtained in a state of high purity, it must be admitted that this has only been achieved recently. Further, it is not quite beyond all doubt whether the purification is really complete even now. The removal of the resins, by the prolonged action of acetone as solvent, is not simple; and the removal of the protein is a far more difficult operation. It has long been recognised that rubber contained two widely different constituents, one soluble, one insoluble, in various organic solvents such as benzene, carbon bisulphide, etc. For some time the amount of this insoluble constituent was greatly exaggerated, some writers going so far as to place the figure at 25 per cent. and even upwards. It was considered by some that the two bodies were isomeric modifications of rubber: bodies which possessed the same composition, but differed in the mode of arrangement of the atoms of carbon and hydrogen. This view was not supported by satisfactory experimental evidence. These supposed isomeric bodies were said to possess properties of opposite nature and to exert different functions in the rubber. The soluble form was a viscous substance, while the insoluble form was of a "nervy" sinewy nature, which imparted strength to the rubber.

It was when matters were in this state that Weber began his important researches on the subject. Beyond what has been said, a number of important data were known, but they lacked coherence.

The composition of rubber had been established by various workers as $C_{10}H_{16}$, as the result of analyses by combustion of the purest specimens of rubber.

The destructive distillation of rubber had been closely

investigated. Among the decomposition products from heated rubber a number of hydrocarbons were isolated. The most important is isoprene, a light, rather pleasant-smelling liquid boiling at about 36°. It has the composition C_5H_8. The constitution, confirmed by synthesis in the laboratory, is

$$\begin{matrix} CH_3 \\ \\ CH_2 \end{matrix} \!\!\!\

saturated by other atoms. A common case is that of a carbon atom which is united to another carbon by a double bond, thus possessing the power of taking up another atom of hydrogen or other monovalent element. It is clear that an unsaturated compound such as this, which is able to take up further atoms of another kind, should on occasion be able to combine with its own molecules. In this way a number of molecules unite to yield a larger molecule. The reverse process is termed "depolymerisation," which consists in the breaking down of a complex molecule into simpler ones of the same composition. This corresponds to the change of ozone into oxygen. It is generally found that cold and pressure favour polymerisation, while heat and reduction of pressure tend to depolymerisation. This is seen in the case of the destructive distillation of rubber, when under the influence of heat the rubber molecules, which are $(C_{10}H_{16})_n$, a polymerised form, break down, yielding the simple C_5H_8 molecules of isoprene. In the case of a colloid, such as rubber, it is very difficult to distinguish between extent of polymerisation and degree of dispersion. Indeed the two are very closely allied, since colloids are precisely those bodies whose particles are of dimensions which place them on the border-line between very fine particles and very large molecules. It will be seen that the difference is very largely one of nomenclature, whether the particles are considered as polymerised molecules, or as aggregations of simple molecules. The point deserves attention, because in rubber literature reference is often made to the "degree of polymerisation" or to the "state of aggregation of the rubber colloid." From what has been said it should be clear that the difference is really one of point of view—in the former case the strictly chemical attitude is taken up, while in the latter the position is considered more in a physical light. It may be added that the second view has much in its favour, since, as Wo. Ostwald has pointed out, it lends itself to more direct measurement, *e.g.*, by determination of the degree of dispersion ultramicroscopically.

We must return to the consideration of the so-called two isomeric modifications—the soluble and insoluble rubber. In view of the contradictory statements extant as to the relative

amounts of these bodies present in raw rubber, Weber re-investigated the question. He found that when rubber was repeatedly treated with acetone to remove the resins and then repeatedly treated with chloroform, a stringy residue was obtained. With Para rubber the quantity of this insoluble substance averaged about 8·5 per cent. Analysis showed that while the soluble part approximated very closely in composition to the formula $C_{10}H_{16}$, especially after purification by fractional treatment of the chloroform solution with alcohol, the insoluble part contained a percentage of carbon and hydrogen which led Weber to ascribe to it the formula $C_{80}H_{68}O_{10}$. It will be seen later that this formula is incorrect, since the presence of a considerable percentage of nitrogen in the body was overlooked. This does not invalidate the conclusion as to the small percentage present of the body itself. Weber stated that "the proportion of the latter is so small that it would be utterly futile to ascribe it to any important, or indeed, distinctly traceable, function as regards the technical aspect of the physical properties of india rubber." Yet from its distribution throughout the rubber, as a reticulated or mesh-like structure, it is conceivable that even this small amount may exert an appreciable influence in the direction of, as it were, holding the material together. At the same time, however, it is true that this mesh structure of protein may, and probably will, be almost destroyed by the severe treatment which rubber undergoes in mixing, so that too much stress ought not to be laid on any strengthening or binding action of the insoluble constituent.

Weber found the greatest difficulty in removing the last traces of rubber from the insoluble matter, and the same tenacity in retaining the rubber was observed by Spence, who worked later on the subject. He showed that the insoluble portion of rubber contained a large amount of nitrogen, and that, far from being an oxidation product of the rubber, it was a protein. He applied the method of silver staining used in microscopy, and was thus able to examine the distribution of the protein, which appeared, dyed black, as a reticulation throughout the rubber. It is now recognised that oxidation products do not normally occur in rubber in large amount.

When speaking as above of the solubility of rubber, the ordinary process of solution is not meant. When a crystalloid, such as salt or sugar, is dissolved in water, solution proceeds to the limit fixed by the solubility of the dissolved substance. Unless supersaturation occurs, this solubility cannot be exceeded. With rubber and other colloids the case is radically different. Although various workers have given data as to the solubility in various solvents, the figures rest on a misconception of the nature of the process of "solution" under these circumstances. As Weber pointed out, rubber does not possess a "solubility" in the ordinary sense of the word, that is, a solubility such as is possessed by crystalloids. What actually occurs when rubber is treated with a solvent is that colloidal swelling takes place. Instead of the rubber passing into the solvent, the exact opposite occurs. The solvent permeates the rubber, which is distended as a jelly-like mass, and becomes more fluid as the quantity of solvent increases. Regarding the rubber as the disperse phase of a colloidal system, we see that at first the rubber, usually termed "solid," is in the form of a gel, in which rubber in the emulsoid phase may be distributed throughout a continuous phase also consisting of rubber. When solvent is added, this passes into the continuous phase, so that, although the amount of solvent may be small, it is regarded as the continuous, not the disperse, phase. The fluid is imagined as, in a sense, filling the pores of the honeycomb structure of rubber. Such an appearance has been observed microscopically in the dilution of jellies by water.

The result of this process further continued is that the mass of rubber originally placed in the solvent is swelled more and more, till at last, as Weber pointed out, the rubber is so fluid that on addition of fresh solvent this is apparently perfectly miscible with the rubber "solution." However, as stated in the last chapter, the colloidal system thus formed will be henceforth called a "solution" for the sake of convenience; when a rubber solution is mentioned it must be understood that the term is meant to be taken with the above reservations.

Largely on account of the difficulty caused by the protein, a rubber may take very long to dissolve. Swelling can only

occur after a certain point by a diffusion of solvent through the cell-like walls of protein. This may be so slow that days are required for complete solution. The solution thus obtained is said to contain particles visible in the ultramicroscope. It is possible that they will not be so easily visible as would be expected from their size, because rubber is an emulsoid colloid, and, as was stated in the last chapter, the index of refraction of the disperse phase is not sufficiently different from that of the medium to render the particles so distinctly visible. The particles are so small that they pass through a paper filter, though filtration is often exceedingly slow, especially with concentrated solutions. This is largely due to clogging of the pores of the paper by the insoluble matter, or by undissolved rubber of a jelly-like consistency. It was stated by Weber that the insoluble matter could only be detected in unwashed rubber, as the treatment on the rollers during washing so disintegrated the insoluble matter that it could not be separated from the solution when the rubber was dissolved. This is true in so far as there is greater difficulty with washed rubber, which has been mechanically worked, but it is still possible to effect a separation even here, though only with more careful filtration or other treatment. It is easy to see that a long continued working between rollers will tend to produce an effect whereby the insoluble matter passes into a state of fine suspension. As has been said, this grades by degrees into colloidal solution.

The swelling process, or solution, is accelerated by shaking, though here again there is the possibility of dividing the insoluble matter too finely. Spence has stated that heating does not exert a marked acceleration of the velocity of solution in solvents such as chloroform, but others do not agree with this conclusion. With solvents of high boiling point, such as toluene or naphtha (a mixture of the three xylenes), there is a tendency at the boiling point to exert a softening action on the rubber.

For the reasons given, filtration is not usually a simple matter in dealing with rubber solutions, and there is much to be said in favour of the view expressed by some workers that it should be abandoned whenever possible in favour of centrifugalisation. A centrifuge should be used capable of dealing with a volume of at

least 50—100 cub. centimetres, working at a fairly high speed. The liquid is whirled for some time, the clear liquid separated by decantation, and washing done by adding repeated quantities of the solvent, whirling, and again decanting till the operation is complete.

A consideration of the solutions of rubber naturally precedes a discussion of the methods adopted for the preparation of the pure substance, rubber itself. This problem is intimately connected with the solution and precipitation of the crude product. This involves a description of the epoch-making researches of Professor C. Harries of Kiel, who has done so much to elucidate the constitution of rubber.

We may pass over the work done by him on technically pure rubber, and begin with the method of purification which he introduced; this is now regarded as standard. The technically pure rubber is extracted with acetone for twenty-four hours; it is then dissolved in benzene; the solution is filtered and poured into alcohol. The precipitated rubber is again extracted with acetone and further treated as above. The whole treatment is carried out three times in all. The rubber so obtained is of very high purity, yielding values for C and H by combustion which approximate very closely to those required by formula.

This substance, pure rubber, has been shown by Harries to be a hydrocarbon which is built up in a way hitherto almost unknown in nature, since the molecule consists of a ring containing eight carbon atoms. The steps by which this conclusion was reached are most interesting, especially since they started out from a research which seemed of a somewhat academic type, and culminated in the artificial production of the rubber hydrocarbon.

Harries had been working on the action of ozone on various unsaturated bodies: he applied the method to elucidate the constitution of oleic acid. He found that, when the substances were treated with ozone, a molecule of ozone added on at each double bond of the main molecule, yielding an ozonide; this ozonide split up on treatment with steam; from the two fractions of the original molecule thus formed it was possible to localise the double bond in the carbon chain, since it was at this point that rupture occurred. The method was successful in the case of

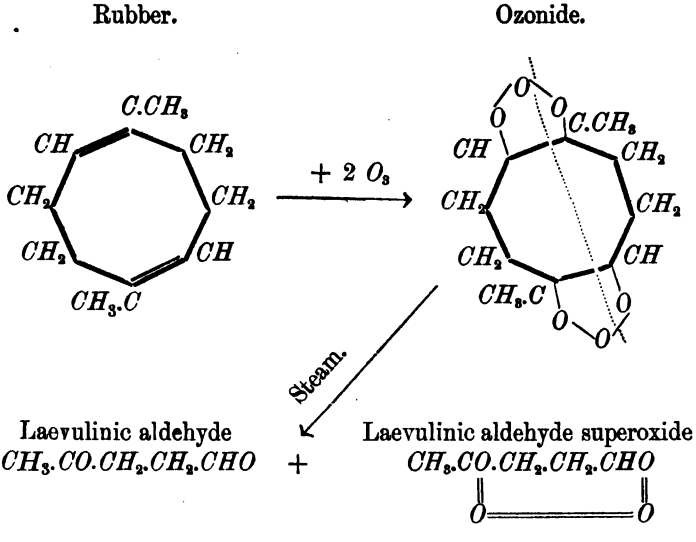
oleic acid, and as rubber possesses two double bonds, the same method was tried. When ozone was bubbled through a solution of rubber in chloroform, an ozonide of the composition $C_{10}H_{16}O_6$ resulted; this body was soluble in chloroform and could thus be separated from the insoluble ozonide formed by rubber resins, though such a procedure was unnecessary in the case of purified rubber. On distillation in steam, the ozonide decomposed. The only products were:—

$CH_3.CO.CH_2.CH_2.CHO$ Laevulinic aldehyde.

$CH_3.CO.CH_2.CH_2.COOH$ Laevulinic acid.

$CH_3.CO.CH_2.CH_2.CHO$
$\|$ $\|$ Laevulinic aldehyde superoxide.
$O=\!=\!=\!=\!=O$

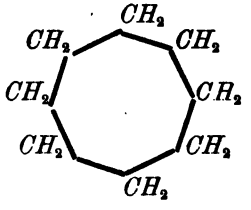
To explain the formation of these products, the following structural formula was put forward for rubber and for its ozonide:—



The break of the ozonide molecule occurs at the dotted line. The laevulinic aldehyde superoxide is considered to contain quadrivalent oxygen. The laevulinic acid which is found results from the aldehyde by the action of water. Thus this classical piece of work leads to the conclusion that the rubber hydro-

carbon contains eight carbon atoms arranged in a ring, in which two double bonds are present, and that two methyl (CH_3) groups are attached to the ring. The correct name for rubber on this basis is "1.5. dimethyl-cyclooctadiene 1.5." "Octadiene" signifies that there are eight members in the ring, and that there are two double bonds, shown by the suffix "-di-ene." The position of these double bonds is indicated by the numbers 1.5. at the end, which signify that they spring from the first and fifth carbon atoms in the ring, if one of these carbons is numbered "1" and the rest are numbered consecutively; "1.5. dimethyl" signifies that two methyl groups are attached to the ring at the positions named.

The rubber hydrocarbon is thus constituted on a characteristic basis. Almost the only, if not the only, other example in nature is the rare one of pseudopelletierin, a substance contained in the bark of the pomegranate tree, which also contains an eight-membered ring. The hydrocarbon octomethylene,

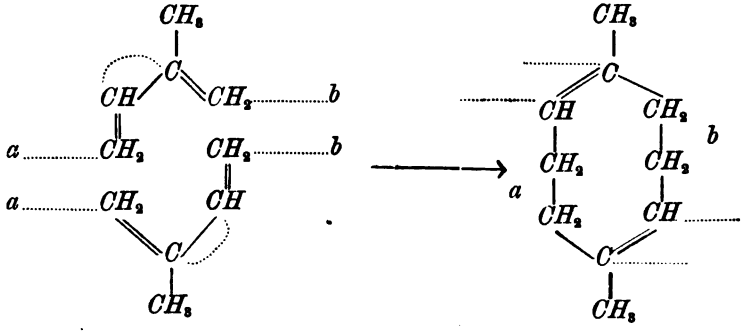


has been obtained from this substance. It may be regarded as the parent substance from which rubber is theoretically derived.

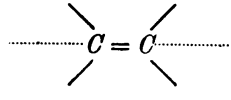
It must be stated that other interpretations have been placed on the work of Harries. Thus, Pickles considers it likely that the rubber molecule may be a large ring, containing a number of $C_{10}H_{16}$ molecules, though with the double bonds and the methyl groups in the positions indicated by Harries. Barrow has suggested that the atoms may be arranged in a spiral form, which would explain certain of the properties. We need not discuss these modifications of the Harries formula here, however.

This work has thus indicated that rubber is not an ordinary open-chain compound, in which the carbon atoms are united as a chain rather than as a ring. The name "polyprene," given by

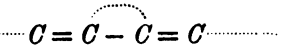
Weber on the assumption that it contains two molecules of isoprene united at the ends, is erroneous. At the same time, the view that rubber could be obtained by the polymerisation of isoprene has been confirmed by Harries and later by others. The transformation comes as a fitting consummation to Harries' brilliant researches. It is true that others had observed it previously. Thus, Tilden found that on long standing isoprene spontaneously polymerised to rubber. The experiment was not susceptible of repetition when desired, and, as Harries remarks, Tilden must have been fortunate in securing conditions which happened to yield the result. Harries himself succeeded in obtaining a good yield by heating the isoprene in a sealed tube with glacial acetic acid, when rubber was obtained as a white elastic solid which answered to the usual tests, yielding the ozonide and other derivatives. Harries explains its formation as occurring thus:—



On the left are represented two molecules of isoprene. The dotted lines indicate "partial valences," on the ingenious theory of Thiele; this theory states that when carbon atoms are united by a double bond the whole of the existing affinity is not expended in the double linkage, but that there is a residual power of binding other atoms. This is expressed by representing "partial valences," which possess the powers of ordinary valences to a more feeble extent, thus:—



When two double bonds are in the position



the partial valences satisfy one another in the centre, and leave the end carbons unsaturated. It is in this way that the benzene ring is considered as saturated, because the partial valences all satisfy one another.

In the diagram for isoprene, it is suggested that the free partial valences, marked *a* and *b*, join up and close the ring. The curved lines show the partial valences which satisfy one another, and thus become ordinary double bonds when the ring is closed. The remaining partial valences may still link with others and thus may explain the polymerisation of the $C_{10}H_{16}$ molecules to $(C_{10}H_{16})_n$.

It is hardly necessary to consider very closely here the question of the synthetic production of rubber on a commercial scale, although one or two points should be mentioned, since the matter is of increasing importance. The process just described is not the only one which professes to solve the problem. Many others have been put forward, starting from isoprene and also from other materials. It is highly doubtful whether many of these will work, but it seems quite certain that some will not.

Some of the more extraordinary of these patents are those in which it is proposed to obtain rubber from various materials by the action of ferments, obtained from rubber or from latex. The majority, however, are alike in that they deal with isoprene. The two main problems are those of cheap production of isoprene, and effective transformation into good quality rubber. Tilden obtained isoprene by the destructive distillation of turpentine. Processes have been patented whereby a better yield is obtained in this way, *e.g.*, that of Heinemann, in which the vapours are passed through a heated structure of copper or silver. Wallace has a patent for the production of isoprene by the dry distillation of the bark of the black-boy tree of Australia. Others again have proposed to obtain isoprene from amyl alcohol, isopentane, etc. The processes are very numerous, but an effective one will have to produce isoprene very cheaply, and it is doubtful whether many of them are capable of doing so for large quantities.

As far as the conversion into rubber is concerned, beyond the process of Harries, there are various others, especially that of Heinemann in which polymerisation is effected by oxygen or ozone. Prolonged heating is usually specified in the processes.

The Baeyer patents deal with the production of rubber, and of allied substances. Taking hydrocarbons differing from isoprene by one or two methyl groups, homologues of rubber are obtained likewise differing from it in the number of methyl groups.

Having shown the constitution and synthesis of rubber, we will return to the properties of the hydrocarbon. The two chief characteristics of rubber are its colloidal nature, and its capacity of reacting as an unsaturated chemical compound, owing to the presence of two double bonds. The compounds formed as derivatives of rubber are usually addition compounds. The $C_{10}H_{16}$ molecule is left intact, but the new body further contains the elements differentiating it from rubber attached to the molecule. Exceptions are known, especially the nitrosite.

Of these derivatives, the first to be considered are those formed by the action of oxygen: they are important not only for their bearing on the life of rubber articles, but because of a certain relationship which appears to exist between them and the rubber resins, though from the researches of Hinrichsen on resins it appears very unlikely that these are derived directly from the rubber. Many years ago, Spiller observed a notable change which had occurred in a sample of rubber which had been exposed to the action of the atmosphere for a number of years. This compound was of a composition not far from that expressed by the formula $C_{10}H_{16}O_8$, and was soluble in alcohol and chloroform. Quite recently the subject has been investigated by Herbst, who passed a continuous stream of air into a boiling solution of rubber in benzene, which was contained in a flask provided with a reflux condenser. The benzene was renewed as required, and after some days the clear yellow solution obtained was distilled down. The residue was soluble in alcohol, and two oxygen derivatives were isolated from it, $C_{10}H_{16}O$ and $C_{10}H_{16}O_3$. Hence this last is similar to the substance examined by Spiller and since called "Spiller's resin." These oxidation products are thus soluble not only in benzene and other rubber solvents but also in alcohol and

other resin solvents, such as acetone. This fact has a very important bearing on rubber analysis, since under certain circumstances rubber shows a much greater tendency to form these products, which are likely to be mistaken for rubber resins. This point will be elaborated later.

The addition compounds formed with sulphur are of fundamental significance in the industry, since their formation is the most plausible explanation of the operation of vulcanisation. The subject is of such magnitude that discussion will be deferred till Chapter V, which deals with it in detail. It will be sufficient to remark here that by the addition of various amounts of sulphur to the rubber nucleus, the properties of the product may be modified to almost any desired extent. This product, vulcanised rubber, is characterised particularly by its enhanced stability against chemical and physical change.

From a purely chemical point of view, the simplest derivative of rubber is the bromine compound. When rubber solutions are treated with bromine, a white precipitate is obtained, possessing the composition $C_{10}H_{16}Br_4$; it is thus a tetrabromide. Two atoms of bromine have added on at each of the two double bonds, yielding a saturated compound, which is fairly stable, though on heating it gives off hydrobromic acid. It can be decomposed by boiling with nitric acid and silver nitrate, though recent work has shown that the reaction is not quite so quantitative as was previously supposed; especially when the nitric acid is at all strong, bromine is lost during boiling. The tetrabromide is interesting because of its comparatively simple chemical nature, and on account of the attention which has been focussed on it from the point of view of analytical determination of rubber in both the raw and vulcanised state.

The behaviour of the other halogens has been studied, and it has even been proposed to vulcanise rubber by their action. Other derivatives have been obtained with the halogen acids. That resulting from hydrochloric acid is interesting; the decomposition of rubber stoppers by this acid must have been frequently observed, but Weber was the first to examine the product. He considered it to consist of addition compounds $C_{10}H_{16}HCl$ and $C_{10}H_{16}2HCl$.

Of the other acids, strong sulphuric has a very destructive action. Concentrated nitric acid also destroys the rubber with extreme rapidity, yielding yellow products containing aromatic acids. On treatment with alkalies they become brown, a reaction which is similar to the well-known xanthoprotein reaction of proteins. The reaction is excessively weighty from the analytical standpoint, since it is the most general method of decomposing rubber when it is desired to oxidise sulphur also.

Alkalies render rubber sticky. Ammonia tends to emulsify it.

By the action of nitrous fumes, various nitro compounds have been obtained, especially by Harries and by Alexander. There has been much discussion as to their suitability for analysis.

Remarkable reactions are shown by a number of chlorine compounds. The action of sulphur chloride, which is one of the most striking, falls under the head of vulcanisation. It has been recently shown by Spence and Galletly that chromyl chloride, CrO_2Cl_2, forms a compound $C_{10}H_{16}$, $2CrO_2Cl_2$, when solutions of rubbers of various botanical origins are mixed with a solution of chromyl chloride in carbon tetrachloride. The compound is rapidly decomposed by moisture and cannot be used in the estimation of rubber.

ANALYSIS.

Loss on Washing.

In considering the analytical problems involved in the examination of raw rubber, the first characteristic number is the **loss on washing**. On large consignments it is best estimated by weighing before, and after, washing and drying. If small samples are to be examined, the loss can still be determined on the large rollers used in actual practice if care is employed, and if a tray is placed beneath, in order to avoid all loss. When the result is required the same day, the washed rubber can be dried on warm rollers, carefully sampled, and a moisture determination made on the sample by heating four hours in gas at 100° C. This method is hardly advisable if further tests are to be done; in this case a portion could be reserved for these tests before drying on hot rollers.

At this point the chemist must decide whether he intends to conduct his analyses on raw rubber as it arrives, or on the technically pure product. Both courses have been recommended, but for the works chemist the author decidedly recommends operating mainly on technically pure rubber, since this is the actual substance which is to be incorporated in the mixings, and sampling can be so readily performed by taking a sample from each washed sheet, mixing these on a pair of clean dry cold rollers, and again selecting a sample of suitable size. For the consulting chemist it may be preferable or necessary to select very carefully a large sample of some lbs. and to wash this in the laboratory on a small washer. But the case is vastly different in a works, where loss on washing can be determined with great accuracy on the large scale. In any case the analysis is best performed on the washed product, and in what follows this will be assumed.

Sampling.

It must be emphasised first that sampling is an operation which requires the utmost care. Naturally the broad principles governing sampling in general will be observed. The sample must be taken from as many places as possible, and to be thoroughly representative of the bulk a large sample should be taken first, mixed, and again sampled. But it is necessary to remember that rubber is not an easy substance to sample. Variations can easily exist, even between adjacent portions of a sheet; consequently it is as well to be rather over-careful in the matter. The warning is necessary, and since accurate sampling is a precursor of all sound analysis, the greatest attention should be devoted to this point, and control experiments should be made to determine whether the chosen method of sampling is actually effective.

Moisture.

The next determination necessary is that of moisture. This should always be estimated, as the presence of more than a certain amount is apt to cause trouble: it leads to "porosity" of the manufactured article. This appears as small pores in the interior, after vulcanisation, and is frequently to be attributed

to moisture. Thus, no rubber should be passed for use unless the moisture content is known. The safe limit varies. For many purposes the rubber should be "bone-dry," often interpreted as about 0·2 per cent. The limit depends materially on the object for which the mixing is designed: thus, if the rubber is to be heavily mechanically treated in the unvulcanised form, more moisture can be allowed, since the opportunity of drying is greater. The numerical limit permissible must be fixed by special requirements.

The estimation of moisture can be performed by several methods. Drying in vacuo over sulphuric acid is accepted as the standard. The finely divided rubber (rolled or cut with sharp scissors) is placed in an exsiccator over sulphuric acid, and dried till the weight is constant. As Korneck has pointed out, twenty-four hours should elapse between the last two weighings. The process may require a number of days. It may be noted that good sulphuric acid must be used (evolving no acid fumes) and must be changed at frequent intervals. The process can be accelerated, as Ditmar recommends, by warming to a moderate temperature in an evacuated tube.

Other methods are more convenient for control purposes. Thus drying may be performed in a stream of coal gas at 100° C. It is simplest to have a water-jacketed oven, provided with an air condenser. A close-fitting gas-tight door should be provided, which can be screwed or bolted up. Through this oven is passed a stream of gas, which may be used for heating afterwards. If the gas supplied is not pure, it may be necessary to wash it first, drying it afterwards. For control purposes, however, the gas need scarcely be specially dried unless it has been washed. There are two possible errors in this method. Rubber possesses the property of absorbing gas, and thus the loss on heating may be less than the true value, or may even change into a gain on heating. On the other hand, especially with rubbers such as Guayule, volatile matter other than moisture may be lost by the rubber. In these cases a correction may be established by comparison with vacuum drying. Since drying for control is done to a certain fixed limit, it is not strictly essential to obtain absolute values so long as the results are concordant. It has been

stated that the method ought to be discarded, since the illuminating constituents of the gas are retained by the rubber. This statement may be correct enough from an academic point of view, but the works chemist requires his results in a reasonable time, and if he can obtain results by gas drying sufficiently close for many requirements, he may still use the method, occasionally checking it by the vacuum method.

The method of Obach, in which the rubber is dried by a stream of dry carbon dioxide or other gas, and the moisture collected in a weighed U-tube containing sulphuric acid, may also be used. In this case the moisture is directly estimated. The rubber itself may also be weighed as a check. The method is not quite so simple as ordinary drying in coal gas, and is thus hardly so convenient for control.

Other methods have been proposed. Drying in air is liable to lead to oxidation of the rubber. The method whereby the wet rubber is extracted with acetone and the moisture determined by drying the residue, adding the weight of resin to it and subtracting from the original weight, is only intended when resin is to be determined also. Even then it cannot be so accurate as direct estimation.

Korneck applied a comparative method which is ingenious, but might give rather high results, as the rubber has to be heated. He swelled the rubber with benzene, distilled off, and dried finally in vacuo over sulphuric acid and paraffin to remove benzene. Here any volatile matter will be estimated as moisture.

* * * * *

The other estimations to be made on technically pure rubber are those of resin, insoluble matter, nitrogen, ash and rubber itself. It may be desirable for certain purposes to estimate a small quantity of sulphur present, but this rarely, if ever, appears in published data.[1] A further estimation necessary in the case of plantation rubber is the qualitative and quantitative examination for traces of the coagulant not removed in washing, such as acetic acid, etc. Beadle and Stevens have published

[1] Values obtained by W. J. Britland and the author for Para rubber are of the order of 0·1 or 0·2 per cent.

estimations of acidity of plantation rubber, and also of raw Para. They found up to about 0·1 per cent. acid (expressed as acetic). In this estimation care must be taken to allow for the acidity of the water used, and to take into account the possibility of traces of alkali from the glass. Jena glassware should be used. Extraction must be repeated. Rubber containing appreciable amounts of free acid should be regarded with suspicion. In the case of Para the acidity mainly, if not entirely, disappears on washing. It has been said that washed Para is even slightly alkaline.

Estimation of Resins.

Resin is almost invariably estimated in modern practice by extraction with acetone. The process of extraction is frequently applied in rubber analysis; some general considerations may be put forward first.

The types of extractor which have been proposed are very numerous. Those of Soxhlet, Zuntz, Weber and Radermacher deserve especial mention. The Soxhlet apparatus is too well known to call for any description. The extractor recommended by Weber simply consists in an outer tube, connected with the neck of the flask, and ending in a reflux condenser, which drips continuously through a smaller inner tube, in which the extraction thimble is placed. The Zuntz apparatus is a compromise between these two types. It consists of an outer tube, between the flask and the reflux, containing an inner tube provided with a syphon, so that the rubber contained therein is extracted on the Soxhlet principle, while maintained always nearly at the boiling point of the solvent. On the whole, the author recommends this type, especially the modification in which connection between the outer tube and the flask is made by a mercury seal, while the outer tube is ground to fit the condenser (as mentioned below). In this form the apparatus will probably have to be made to order, but this is of course very simple.

As in all forms of washing, a greater effect is obtained by frequent action of a small volume than by more prolonged action of a larger volume. Hence the capacity of the extractor should be as small as possible compatible with the use of sufficient

material. Drainage should be as complete as possible, so that it is better to place the rubber straight in the extractor without using a paper thimble. If the rubber is resinous and liable to melt together by the heat, it must be rolled in strips of fat-free filter-paper. The solvent is best maintained near its boiling point. This is attained in those forms of extractor in which the actual extraction tube is surrounded by the vapours of the solvent. Technically pure acetone, redistilled if necessary, is satisfactory as solvent. As acetone dissolves sulphur and resins from rubber, and a white aromatic smelling body from corks, it is necessary for accurate work to use apparatus in which all joints are ground-glass, or mercury seals. The use of mercury seals is very convenient, since the flasks are all interchangeable. Care is necessary in order to avoid spilling the mercury in the flask, and in removing all mercury before weighing, and it is not so easy to distil down or to dry the flask. In spite of these small difficulties it will be found an immense saving of time to have flasks which can be used at once on any extractor. The joint between extractor and condenser may more conveniently be glass, since these form a pair not likely to be broken.

The rubber should be as finely divided as possible. While vulcanised rubber can be obtained as a powder by "crumbing" it, this is impossible with raw rubber except by freezing it, say in liquid air, and then pulverising or filing it. At that low temperature it is very brittle. In ordinary cases the rubber is either cut up very finely or, better, rolled into a thin sheet. This can be done on a small pair of laboratory rollers. If possible, these should be installed with a belt connected to the nearest shafting, as much time can thus be saved in the preparation of samples for analysis. Such rollers form an essential appliance in the rubber laboratory. If power is not available, they may be made slightly smaller, and hand worked. They are best fixed not in the main laboratory, so that they do not rust because of acid fumes.

The duration of extraction is a very important point. It has been emphasised by various workers that, to obtain accurate results, it is necessary to continue extraction till it is shown that

all resin is actually removed. The first numerical data as to the time actually required for complete extraction appear to be those of Zilchert, who examined about seventeen samples of various raw rubbers.

The rubber, cut into thin strips, was placed in a Radermacher extractor. Ten grammes were taken in each case. Extraction was continued with periodic changes of the flask, at first every hour, then every two to three hours. It was assumed that extraction was complete when two hours' extraction only removed 0·01 per cent. resin, *i.e.*, 1 milligram. For some samples, 32 hours were required. It was found that results sufficiently accurate for technical purposes were obtained by an extraction of ten hours provided that the extractor works vigorously. Even after this period of time, however, in one case there yet remained 7 per cent. of the total amount of resin present, which meant an error of over 1 per cent. on the 14 per cent. found. Nevertheless, ten hours is to be recommended for ordinary work, with the precaution of applying a check flask or flasks in important cases. It has been recommended to protect the apparatus from direct light: this is an advisable precaution in order to preclude any acceleration of oxidation by light.

The resin is weighed by distilling off the acetone and drying to constant weight at 105° C. Before placing in the desiccator a stream of air is gently blown through the flask. This may also be done from time to time during drying. The flask itself may lose about half a milligram or less during extraction, by the solvent action of the water in the bath. This is usually immaterial. The flask must not be rubbed immediately before weighing, or the apparent weight will be smaller than the correct weight, owing to electrification of the glass. This error may amount to a milligram upwards.

An important question is that of the drying of the raw rubber before extraction. In the method of Jules Jacobsen, the rubber is not dried, but weighed after extraction. From the point of view of rapidity of execution, there is much in favour of this method, even though it is not quite so accurate for the moisture. The best method is that of drying the rubber in vacuo before extraction, but this is an extremely lengthy process sometimes.

Again, the wet rubber can be extracted, and moisture determined on an accurately taken sample. Finally, despite the condemnation of Ditmar, the rubber may be dried for extraction at 100° C., and this method has much in its favour for rapid technical work. Ditmar states that he dried two samples of rubber in an oven, and found the acetone extract increased enormously. The present author, using coal gas, has not had this experience; whether Ditmar dried in air, thus leading to the formation of soluble oxidation products, is not clear from the statement in his book. At all events, drying for not too long in coal-gas, the author has not found any such abnormal results.

There are other methods of resin estimation which will be considered in connection with the estimation of rubber. The general method is that of acetone extraction, although some workers have used other solvents, such as absolute alcohol. A peculiar form of extraction apparatus used by Pontio may be mentioned. He calls it a digestor-lixiviator. The sample is weighed out and suspended in a large vessel of boiling solvent for some time. Then it is placed in a funnel under a rose, at the top of the apparatus, and extracted some hours. At the end of the time fixed it is dried and weighed. Six simultaneous estimations can be made in the apparatus; there are six roses attached to condensers.

The percentage of resin is, within certain limits, characteristic for a brand of raw rubber. The nature of the resin has been little investigated chemically. Part of it can usually be saponified; part cannot. In general the estimation of the saponifiable fraction is unnecessary. Hinrichsen and Kindscher have examined a number of rubber resins in this way, also measuring their iodine values. The results need not be considered here. They further examined the optical activity of the resins. These were dissolved in benzene, and the rotation determined in a polarimeter. The remarkable fact was discovered that all rubbers yield optically active resins, with the exceptions of Para (wild and plantation) and a less important rubber; the same phenomenon was observed with the resins from vulcanised rubber. In this way it was possible to detect the presence of rubber other than Para in a mixing, since if there is optical

activity, other rubbers must be present. The converse is frequently, but not universally, true. The interesting theoretical conclusion was drawn that, since the rubber molecule does not contain an asymmetric carbon atom (one united to four different groups, which causes optical activity), the resins, at all events that portion of them which is optically active, are not directly derived from the rubber itself.

Tables containing the percentages of resin in various raw rubbers can be found in most of the larger works of reference. The object of the estimation of resin is to see whether samples submitted conform to the normal standard which will be established for each grade of rubber regularly bought. It is to be noted that the old figure of 1·2 per cent. resin in Para is now rejected, and for technically pure Para rubber 3 per cent. is a more general figure. It is not possible to conclude definitely from the amount of acetone extract what raw rubber is under consideration, especially now that deresinified rubbers, which have undergone partial removal of resins on a large scale, are on the market. The effect of the resin on the quality of the rubber depends greatly on the kind of resin. Nevertheless the estimation of resin is advisable, since it may give useful indications. Speaking generally, the lower the percentage of resin, and the harder the resin, the better is the quality of the rubber.

Insoluble Matter.

The estimation of insoluble matter, which includes both inorganic and organic impurities—ash and protein—is performed by treating with a suitable solvent, and separating the solution by filtration, or by standing only or by the use of the centrifuge. A number of solvents may be used; choice will depend on the operations which are to be performed afterwards. If a high boiling solvent, such as naphtha, is used at the boiling-point, solution proceeds with comparative ease, but it is difficult to obtain the rubber from the solution afterwards. On the other hand, if a low boiling solvent such as benzene or chloroform is used, solution occurs with extreme slowness in many cases. Spence stated that the velocity of solution was not materially accelerated by boiling, as a rule. This conclusion is not generally accepted, however.

He prescribed treatment with these solvents till solution is complete, without specifying any definite time, which indeed would be impossible. However, days may be required, so that the process does not appeal to the worker who wishes for a rapid routine test. Apart from this, it is somewhat unsatisfactory, as it is difficult to know when solution is complete.

Fendler has recently recommended toluene as solvent. He states that the solutions thus obtained (by heating in a boiling water bath) are usually so slightly viscous that the separation can be effected by decantation. In an obstinate case he effected separation by centrifugalising for one hour at 1,000 revolutions. He considers that centrifugalisation of the toluene solution is likely to be a useful general method.

For reasons which will be given later, the present author attaches more importance at the present juncture to the determination of insoluble matter than to that of rubber itself. Consequently those solvents are recommended which dissolve rubber more effectively, *i.e.*, the high-boiling solvents, such as naphtha (a mixture of xylenes) or toluene, even if they do yield a solution from which it is difficult to precipitate the rubber.

Pontio suggests xylene as solvent, and others have used the same solvent. For determination of insoluble matter, when it is not desired to proceed further with the rubber solution, the use of naphtha, boiling if necessary, has much in its favour. Filtration can be done through a weighed Gooch crucible filled with asbestos, or if this is too close, with glass wool. The residue is washed with naphtha, then with petroleum ether, and dried in an air oven till constant in weight.

Gooch crucibles are capable of wide application in rubber analysis. The asbestos used should be very carefully selected, and if necessary purified by boiling with aqua regia. If good asbestos is used, it is possible to ignite the dry crucible without serious loss of weight. In this way the amount of inorganic matter in the insoluble matter can be determined, and compared with the result obtained by ashing (see later). When drying Gooch crucibles, it is recommended to moisten the asbestos with the solvent which is to be used subsequently (in the above case petroleum ether) and to dry at a definite temperature.

If glass wool is used, it can be packed in a tube. The glass wool must be very carefully selected, as poorer qualities easily lose particles of glass. Filtration through paper is laborious, unless very dilute solutions are used. Moreover, although weighing filter paper to constancy is a well-recognised analytical operation, it is nevertheless a troublesome one. If paper is used, it should be well wetted with the solvent to be used later, before it is placed in the oven.

Nitrogen.

Nitrogen is estimated by the usual Kjeldahl process:[1] 1—2 grammes rubber are placed in a 500—600 cub. centimetre Kjeldahl flask; 20 cub. centimetres of a mixture of 3 volumes conc. and 2 volumes pure fuming sulphuric acid are added, together with one drop of mercury. Heating is continued on a sand bath till the solution is clear and completely colourless. In presence of iron compounds the liquid is occasionally faintly yellow. After cooling, the liquid is diluted with 250 cub. centimetres water, washing down the flask. When again cool, 80 cub. centimetres of caustic soda (sp. gr. 1·35) (free from nitrates) are added, and as much potassium sulphide solution (40 grammes commercial salt per litre) till all the mercury is precipitated and the liquid appears black. 25 cub. centimetres may be required.

A little zinc powder is added, and the flask is rapidly connected with the distillation tube. The liquid is distilled, till about 100 cub. centimetres have passed over, into $\frac{N}{1}$ sulphuric acid. The excess of acid at the end of the operation is determined by titration with $\frac{N}{10}$ baryta, using methyl orange. The nitrogen is calculated from the ammonia evolved.

One per cent. nitrogen is usually considered to be equivalent to 6·25 per cent. protein, when working on washed rubber. Unwashed rubber contains bodies richer in nitrogen.

Ash.

Ash is estimated by charring about 2 grammes of rubber in a porcelain or platinum crucible, best in small pieces at a time,

[1] Ditmar. Analyse des Kautschuks, 1909, p. 167.

and gently igniting the residue. To prevent the rubber catching fire it is advisable to place the crucible in a hole cut out of an asbestos sheet, so that the gas flame cannot set fire to the volatile products. The carbon can be readily burnt off at a gentle heat in the muffle. Good washed rubber does not contain much ash. In Para it may be as low as 0·2 per cent. A qualitative examination may be made. The following are frequently present: *Ca, Mg, Fe,* phosphates, sulphates, etc. It may be possible to draw some conclusions as to the origin of the rubber from the elements present in the ash.

Estimation of Rubber.

Lastly, there is the estimation of the rubber hydrocarbon itself. The importance of this is, in one sense, obvious. In another sense however, it must, or it should, be candidly admitted that at the present time this is exaggerated by certain writers. While it certainly is important to know how much rubber one is obtaining at a given price—a consideration which is especially important in comparing low-grade variable rubbers—it must be said that the case is entirely and absolutely different for hard fine Para, even when this is being compared with first latex plantation Para. In these cases, as far as present knowledge goes, the slight variations in the rubber content are no index of the value. In other words, at present we are unable to correlate the percentage of rubber with the physical properties of the product. It is much more true that some correlation will be found, and, indeed, is found to an extent, between the precise colloidal nature of the rubber itself (perhaps from its degree of dispersion, and probably by methods such as viscosity determination) and the properties of the material. The amount and nature of the impurities also lead to more direct information.

Yet the determination of the actual amount of rubber present cannot be regarded as unimportant. All that has been said above is only designed to hint that for the technical chemist, at all events for him who desires a routine test to be applied in the valuation of raw rubber, this particular estimation hardly possesses the importance which might be imagined at first. For if the technical chemist obtains such percentages of rubber,

he will be unable to interpret them satisfactorily. This is as far as routine only is concerned. From a research point of view (and also when fresh samples of new rubbers are to be examined) the determination is necessary, especially since the determination of rubber in vulcanised rubber goods—a most important estimation—must of necessity be based on a knowledge of the raw product.

Difference Method.

Much has been written on the various methods which have been proposed. The first and most evident is the "difference method," in which rubber is estimated by difference, after determining all the other constituents. Various writers have condemned it as obsolete, yet it almost appears that a reaction is now setting in. In the present author's opinion, it is merely shutting one's eyes to facts to decry the method as of "purely historical interest." When we consider the various methods which have been proposed to supersede this so-called "obsolete" difference method, we find that they yield results differing considerably among one another and even among themselves (though it has been suggested that some of these discrepancies in duplicate estimations by the same method may be due to insufficient sampling).

Practically all the methods suffer from the difficulty of satisfactory separation of rubber and insoluble matter. In the difference method, moisture, resin, insoluble matter (ash and protein) are estimated, and the sum deducted from 100 per cent. Unless the treatment with naphtha is considered as being violent enough to decompose the protein, which is improbable, or unless it yields unfilterable solutions, it appears evident that a more accurate result can be obtained at present by this method, in which the insoluble matter can be rigorously treated to free it from rubber, than by a method in which separation is effected by a tedious treatment with a low-boiling solvent. In the latter case the rubber is estimated by various methods (which yield discordant results very often). Apart from sentimental considerations, the only really sound objection to the difference method would be the proof of the presence of non-rubber sub-

stances other than those we normally estimate. But as far as we know at present, the substances which have been mentioned are the only normal constituents occurring in fair amounts, with the exception of sugars. If these are present in fair amount in a given sample (it has been mentioned that they have been found in washed rubber) they should be estimated, and also estimated in the insoluble, in case they have not been completely separated. The case is not one usually considered, however.

In short, working by the difference method the crucial separation—insoluble matter from soluble matter—can be effected with greater ease when there is a latitude in the choice of solvent. In the direct method this choice is limited by the exigencies of ease of removal afterwards and so on.

The main disadvantage of the difference method, and one upon which its opponents lay great stress, is that the errors of the other determinations are "heaped up" in the rubber estimation. Seeing that this is usually by far the largest percentage, that the other percentages are small and not many in number, and that they are all more easily (and therefore probably more accurately) obtained, this objection carries very little weight at the present time.

Despite this, however, direct estimation has of course advantages from a scientific point of view, and it must be clearly understood that the above observations only relate to the state of affairs now prevailing. It is by no means intended to deny that direct determination would be the ideal, if it were possible.

Method of Spence.

These matters have occupied the attention of Korneck, in a recent research entitled "Critical Investigations on the Analytical Problems of Raw Rubber." He takes as a standard the method proposed by Spence. The rubber is extracted with acetone, and dried over sulphuric acid and paraffin wax in vacuo. [It may be noted that $NaOH$ ought to be present, since SO_2 may result by the action of the acetone on the acid. Rubber is known to absorb SO_2.] When dry, solution is accomplished in benzene or chloroform without limiting the time required for complete

solution, which may be considerable. The solution is made up to a definite volume, and filtered. To save time, an aliquot part is taken from the filtrate. This is evaporated down in a weighed flask and dried. The remainder of the solution is diluted so that it will filter more rapidly, and the insoluble matter is finally washed. It will be seen that although this is termed a "direct" method, and was accepted as a standard by Korneck, it is bound to give the same result as the difference method with accurate work. If unknown substances (non-volatile) are present they will vitiate the result by this method precisely to the extent of their effect on the difference method!

The essential point of the method is that involved in the phrase "without limitation of time." If, as the method prescribes, *complete solution* occurs, the result will be satisfactory. This is exactly the point which causes so much difficulty throughout. It is stated that complete solution may occur in a few hours, but may require days, which is not promising from a technical standpoint.

Fendler's Method.

A cognate type of method, which at one time enjoyed considerable vogue, is that in which the rubber is dissolved out and then precipitated. We need not consider the fractional precipitation method of Schneider, which may be regarded as obsolete. Fendler's alcohol precipitation method is the important one of this type. The rubber is treated with a solvent, such as petroleum ether or carbon tetrachloride, for a certain time, often two days. The solution is filtered, and an aliquot part of the solution shaken vigorously with excess of alcohol. The rubber is precipitated as a clot: the resin remains dissolved. After kneading the rubber in alcohol and washing the flask, flask and rubber are dried and weighed. Evaporation of the liquid gives the resin.

It has since been shown, by Fendler himself and by others, that:—

(1) Solution is frequently incomplete within a fixed short period, *e.g.*, two days. This is, of course, the fundamental difficulty discussed already.

(2) In some cases all the rubber is not precipitated.

(3) The precipitated rubber contains some resin.

The method has been employed in a modified form by Bourne for resin estimation. However, although errors (2) and (3) may balance one another, the method is rarely used now, chiefly because of the difficulty of incomplete solution in the solvents chosen.

Tetrabromide Methods.

We come finally to methods in which the rubber is determined by transforming it into some suitable derivative, and weighing as such. The derivatives employed for this purpose are the tetrabromide and the nitrosite.

Budde first proposed the tetrabromide method in a workable form. In his first process, 1 gramme of rubber is covered with carbon tetrachloride in a 100 cub. centimetre flask, and allowed to stand, with repeated shaking, until the rubber is dissolved. The liquid is then made up to 100 cub. centimetres, and well shaken. Ten cub. centimetres are taken, filtered if necessary, diluting with carbon tetrachloride, and 50 cub. centimetres of the bromination liquid are added. [This consists of 16 grammes (= 6 cub. centimetres) bromine, and 1 gramme iodine in 1 litre carbon tetrachloride.] The liquid soon becomes turbid; when it is again clear half the volume of alcohol is added. The liquid becomes light yellow in colour; the alcohol serves to harden the precipitate (probably a sort of coagulative action is exerted). The precipitate is collected on a weighed filter, washed first with a mixture of 2 parts carbon tetrachloride + 1 part alcohol, and finally with alcohol alone. It is then dried to constant weight at 50°—60° C.

$C_{10}H_{16}Br_4$ (456) corresponds to $C_{10}H_{16}$ (136).

Other methods have been proposed by Budde; the question will arise again in dealing with the analysis of vulcanised rubber. The process above has been modified by Fendler and Kühn, since it does not afford sufficient assurance as to solubility of rubber or as to complete bromination. It may be noted here that the presence of protein is liable to lead to errors, since Spence showed that bromination products could be obtained from

proteins under the conditions of these processes. Fendler and Kühn proceed thus[1]:—

About 1 gramme of the finely divided rubber is covered with 60 cub. centimetres toluene in a 100 cub. centimetre flask. The flask is placed in a boiling-water bath and repeatedly shaken, each time inserting the stopper. After some time the rubber dissolves. After cooling, the liquid is made up to 100 cub. centimetres. The solution is usually so slightly viscous that insoluble matter settles at once. Ten cub. centimetres of the filtrate are measured out accurately in a small cylinder graduated to $\frac{1}{10}$ cub. centimetre. The liquid is rinsed out with carbon tetrachloride into a 200 cub. centimetre beaker. This is hung in a boiling-water bath, so that it is completely surrounded by vapour. After about half an hour the liquid has evaporated; it is not heated longer than necessary. The residue is then stirred with 50 cub. centimetres carbon tetrachloride, when approximately complete solution occurs. 50 cub. centimetres of the bromination liquid (as before) are added, and the mixture is allowed to stand for twenty-four hours. 50 cub. centimetres absolute alcohol are added; the liquid is stirred vigorously to obtain the precipitate in easily filterable form. This is collected on a weighed filter, washed with a mixture of 2 parts tetrachloride and 1 part alcohol, then with alcohol alone, and finally dried at 50°—60° C.

Although this method has certain disadvantages, it appears promising on the whole, though Korneck does not consider it very closely. Fendler is inclined to recommend solution of the raw rubber in toluene and separation by centrifugalisation as a general method, as mentioned above.

Budde's other methods involve volumetric estimation of the bromine in the tetrabromide, by heating with excess of silver nitrate in presence of nitric acid. Spence, Galletly and Scott have criticised the foundation of this method, showing that bromine is lost under certain conditions. Other methods have been proposed to replace this, which will be considered later.

The tetrabromide method for raw rubber is interesting, but it cannot be considered that finality has been reached yet.

[1] For this and other of these methods a useful summary by Fendler, reprinted from the *Gummi Zeitung*, has been consulted among other works.

Nitrosite Method.

The nitrosite method has been investigated chiefly by Harries, Fendler, Alexander, and Korneck. It essentially depends on the production of a body (either $C_{10}H_{15}N_3O_7$, the nitrosite "c" of Harries, or $C_9H_{12}N_2O_6$ according to Alexander), by passing nitrous fumes into a solution of the rubber, usually in benzene. The subsequent treatment of the precipitated nitrosite varies in the different methods. Although it has been criticised by Fendler, the form given by Korneck (who worked with Harries) appears to yield good results.[1] One gramme of the rubber, best acetone extracted, is swollen with benzene. Nitrous fumes, generated by the action of nitric acid (sp. gr. 1·3) on arsenic trioxide in lumps the size of hazel-nuts, and dried by passage through a tower of phosphorus pentoxide, are led into the solution for one hour. The leading tube (which should be wide, so that it will not be stopped up) and the beaker containing the solution are previously weighed. After standing for a short time, the clear liquid is decanted through a weighed Gooch crucible, which is washed with benzene. Seventy-five cub. centimetres of fresh benzene are added, nitrous fumes passed for half an hour, and the liquid allowed to stand over night. It is then decanted through the Gooch crucible and washing is performed, first with benzene, finally with absolute ether. Beaker, tube and crucible are placed half an hour in an exsiccator to remove ether, and then dried in an air oven at 80° C. The rubber nitrosite is then dissolved out by washing with acetone, and beaker, tube and crucible are again dried and weighed. The difference in the weights represents rubber nitrosite.

$$\text{Rubber} = \text{nitrosite} \times \frac{136}{289}.$$

Under the conditions prescribed by Alexander, the compound $C_9H_{12}N_2O_6$ results. He has shown that carbon dioxide is lost in the formation of this body from $C_{10}H_{16}$. He considers that this body is also formed in the ordinary nitrosite processes, explaining the loss on heating to 80° as due to this. Alexander's method will be mentioned later. Older forms of the nitrosite method

[1] *Gummi Zeit.*, 1910. Abstract *Journ. Soc. Chem. Ind.*, 1910, 1321.

yielded results which were too high, but Korneck found that the above method gave results concordant with the method of Spence.

* * * * *

Viscosity Measurements.

It remains to mention the viscosity test. It has been found that ordinary chemical analysis affords no sound indication of the relative value of plantation Para samples. The method which is nearest to the requirements of actual practice is that in which the rubber is vulcanised, and tested afterwards. The technique of vulcanisation will be considered in Chapter V. The other method, which has been found to yield indications of the value of the rubber, is that in which the viscosity of the solutions is measured. The question has been investigated by Axelrod, Schidrowitz, and Marckwald and Frank. Two main types of viscometer have been used. Those of the efflux type have the disadvantage of being affected by eddy currents, and Schidrowitz uses the Ostwald form, in which two bulbs are connected by a long narrow capillary. The time required for the flow of a definite volume is measured. More than one estimation is really necessary, since any trace of dust lowers the velocity of flow and thus apparently raises the viscosity. Resins affect the result. Schidrowitz recommends extraction with acetone, solution by boiling on the reflux with benzene, and allowing the liquid to stand. If necessary the solution is filtered. The strength of the solution is determined by evaporation of a known amount. The viscosity must be measured for a number of concentrations, and a curve plotted. A tangent is drawn to this curve at 1 per cent. rubber, and from this line the value for 100 per cent. rubber is calculated.

Marckwald and Frank use an efflux viscometer, in which a definite volume of the naphtha solution is allowed to flow through an orifice in a pear-shaped vessel.

It is concluded that, for rubbers of the same botanical class, the goodness of the rubber is dependent on the viscosity —high viscosity, good quality. Schidrowitz states that, in general, existing differences are enhanced by heating the

rubber previously, which is no disadvantage from a technical standpoint.[1]

The theoretical basis of the viscosity method is not yet clear. F. D. Farrow and the present author have examined solutions of measured viscosity in the ultramicroscope, in order to see whether high viscosity corresponds with low degree of dispersion. To the present, however, perhaps because the particles may become invisible on dilution (see p. 18) no conclusion has been reached.

LITERATURE.

"The Chemistry of India Rubber," by Weber; "Rubber," by Schidrowitz; "Analyse des Kautschuks," by Ditmar; "Analyse du Caoutchouc et de la Gutta-percha," by Pontio; "Der Kautschuk und seine Prüfung," by Hinrichsen and Memmler; "India Rubber and its Manufacture," by Terry, and other works. There are numerous journals: *Gummi Zeitung* (Berlin); *Gummi Markt* (Hamburg); *India Rubber World* (New York); *Le Caoutchouc et la Gutta-percha* (Paris); *India Rubber Journal* (London); *Rubber World* (London); *Journal of Soc. of Chem. Industry* (London), (Abstracts). Most of the original work finds its way into the last three journals. It is recommended that their indexes should be consulted for details as to any work to which reference has been made in this and succeeding chapters. See also "The Rubber Industry" (report of 1911 Rubber Exhibition).

[1] *India Rubber Journal*, 1911, Marckwald and Frank. *J. S. C. I.*, 1909, p. 3, Schidrowitz, and in "The Rubber Industry."

CHAPTER III

GUTTA-PERCHA AND BALATA

GUTTA-PERCHA and balata are likewise obtained from latices of various trees, which grow much more slowly than rubber trees, so that culture in plantations, unless carried out by Government effort, is a very serious problem. The method of extraction practised by natives was extremely barbarous, merely consisting in cutting down the whole tree, somewhat in the same way as Guayule. Efforts have been made to render this wasteful procedure impossible: the alternative is to tap, or to remove the leaves and branches. The gutta is extracted sometimes by solvents.

Outwardly, these substances are distinguished primarily from rubber by possessing plasticity rather than elasticity. They are employed in the unvulcanised state, as, though vulcanisation is possible, it does not exert a beneficial influence. On account of their imperviousness to water, they are largely used for the insulation of deep-sea cables.

The resin content varies enormously, and is usually much higher than that of rubber. Cheaper qualities, containing very high percentages of resin, are often partially deresinified by treatment with cold petrol, which dissolves the resins and not the gutta (hot petrol will dissolve the gutta also).

As far as the hydrocarbon is concerned, they both contain a body of the composition $C_{10}H_{16}$, which Harries has shown, in the case of gutta-percha, to yield similar results to rubber on ozonisation. The constitution is probably very similar. Other derivatives of this hydrocarbon have been closely investigated by Caspari, who found that they also were very similar to those of rubber. A purely chemical distinction between these bodies and rubber is thus not existent.

The resins contained in gutta-percha and balata are of two

classes, the albanes and the fluaviles, one soluble in hot, the other in cold, alcohol.

The valuation of these bodies is mainly concerned with the resin content. This is usually estimated by extraction with cold ether. The finely divided sample is allowed to stand for some hours with successive portions of ether, and the resin is determined by difference, the gutta being dried to constant weight.

Insoluble matter is best determined by solution in benzene or chloroform, and filtration through a Gooch crucible.

Moisture can be determined by heating in gas, or in a current of dry carbon dioxide, weighing the moisture carried over, and also weighing the gutta before and after (Obach).

The percentage of the **hydrocarbon (gutta)** present may be estimated by solution in benzene, filtration, and precipitation by alcohol. The method is not really accurate, since, as has been shown by Caspari and others, resin is retained in the gutta, while a certain amount of the latter may remain suspended in the liquid.

Accordingly, the usual estimations are those of moisture, insoluble matter, and resin by the cold ether extract.

LITERATURE.

"Die Gutta-percha," by Obach; "Cantor Lectures," by Obach; *Jahrbuch der Kautschuk Industrie*, 1908, Gottlob; *Journ. Soc. Chem. Ind.*, 1905, 1274, Caspari.

CHAPTER IV

MIXING

Rubber manufacture has been defined as the "art of compounding," and the definition is sound in so far as it emphasises the enormous importance of judicious mixing. It is not enough to use good raw rubber: it is necessary to select the most suitable compounding ingredients which will yield a mixing best satisfying the requirements as to various properties at the required price, if a limit is fixed.

The designing of mixings must necessarily be largely a matter of experience, supplemented by scientifically thought-out experiments. Chemical work comes into play in rigorously controlling the quality of the raw materials used, not only for absence of deleterious constituents, but also for constancy of composition, without which it is difficult to obtain concordant results in the later stages of manufacture. This routine work is of prime importance; it will be considered after the description of the various ingredients.

Beyond this, however, the efficiency of the actual mixing process requires to be controlled by periodic estimations of ash, or of sulphur, on some mixing which is being done in the ordinary way. Several samples should be tested, taken from various parts of the compounded rubber, at various stages during mixing, and also after mixing. As well as this, it may be advisable to examine small portions for homogeneity by taking the ash on neighbouring samples which are very small in bulk, as low as 0·1 grammes. If larger samples such as 1 gramme are exclusively examined, there is a danger of missing local inequalities. Finally, microscopical examinations should be made from time to time. Of course, all powders used in mixing should be well sieved and perfectly dry; if not, lumps can be detected in the mixing.

Lastly, the chemist may be reminded of the wide field which lies open in the direction of curing faults by altering existing mixings. Here the fundamental principle (unless, of course, one is working by instinct) is to change only one variable at a time, and to check carefully the influence of all possible factors. In a complex process like the vulcanisation of an ordinary rubber mix, it is unsafe to make almost any assumptions as to what will happen precisely, when any variables are altered, unless this is controlled by trial. It is, of course, very tempting when a mixing does not give satisfactory results, to alter two or three variables in the hope of attaining the desired result. Nevertheless, if the alterations are made more systematically and more gradually, much will be learnt about the cause of the trouble, so that it will be possible to diagnose it on a future occasion.

* * * * *

The proportion and nature of the ingredients being once determined, the operation of mixing is performed as follows:— The raw rubber is masticated, *i.e.*, worked on unequal speed rollers till it is of a suitable consistency to receive the powders. These rollers are heated or cooled by steam or water. Wax or similar ingredients which exert a softening influence are added before the powders. These are then gradually mixed in. In some cases sulphur is mixed with the powders; in other cases, it is added separately just at the end of the operation. Practice varies, depending partly on the nature of the mix. If there is much liability to "vulcanisation on the rolls" (a superficial but troublesome effect due to overheating a readily curing mix), it may be advisable to add the sulphur separately.

* * * * *

The compounding ingredients used in conjunction with rubber may be classified in various ways. Arranging them according to their function we have:—

(1) Vulcanising.—Sulphur. Also certain sulphides, on account of the free sulphur which they contain.

(2) Modifying the properties of the rubber.—This comprises the true filling materials, added for the sake of their effect on the rubber, not for mere weight. They alter colour, hardness, strength, etc.

(3) Bulking.—Various mineral fillers increasing bulk and thus lowering price.

(4) Substituent.—Organic materials of pseudo-rubbery qualities to a greater or less extent.

(5) Medicinal.—Ingredients added to cure certain defects, etc. Especially those added to accelerate vulcanisation.

It is not easy to discuss the compounding ingredients in this order, since most of them exert more than one function. For our purpose we will consider first the organic and then the inorganic ingredients. For the sake of simplicity, the analytical notes on each ingredient will be given after the description, instead of at the end of the chapter. It is hardly possible to give a complete list of the substances which have been suggested or used as ingredients of a rubber mixing. The most diverse have attracted attention; it is sufficient here to consider the more important. Organic fillers may be divided into four groups.

(1) Waste rubber and Reclaimed rubber.

(2) The so-called Rubber Substitutes of all kinds.

(3) Other organic fillers (bulk, etc.).

(4) Ingredients added for some other specific purpose.

It should be emphasised at the outset that it is a great mistake to suppose that a mixing is bad because it contains these fillers. The mistake certainly is not one which would be made by the experienced, but it is very prevalent in certain circles. For many articles it is absolutely unnecessary to use "nothing but Para." Other raw rubbers have their own sphere of usefulness, and it is wasteful to use a more valuable rubber when a cheaper one would suffice. The choice of the brand of raw rubber to be used demands wide experience, and is dependent on the peculiar factors of the individual case. It should be noted, however, that it is well to bear closely in mind the possibilty of obtaining a steady supply of the rubber chosen, which supply will be of constant properties, especially speed of vulcanisation. This point has been mentioned in Chapter II; it is one which has attracted much attention in the case of plantation rubber especially.

In the same way, when certain properties are desired at a certain price, it may be impossible to meet these requirements by the use of rubber alone. In these cases, then, it is the legitimate

and indeed the only solution to use organic fillers such as those which have been mentioned. Provided discretion is exercised, the claims of efficiency can be met in very many cases.

Waste Rubber and Reclaimed Rubber.

These fillers are practically exclusively employed for the purpose of lowering the price of a mixing. When this can be done without prejudicing the quality, as it can for many articles, or when the price is all important, it is clear that their use is of great value.

Huge quantities of waste rubber are available. In some cases it is re-formed, by processes involving the use of heat and great pressure, whereby the article is moulded direct. The majority of the material is first treated in various ways and is then incorporated into fresh mixings. When waste rubber is employed as such, it often consists of selected and graded waste which is cut into extremely fine shreds. This **Shredded Waste** replaces a certain amount of raw rubber. Other ingredients such as wax may be necessary to soften it. When fresh grades of this material are bought, a thorough chemical examination should be made, and this also applies to the control of successive deliveries. The tests used are the same as for reclaimed rubber (see later).

Reclaimed Rubber.

The following remarks are partially based on an excellent account of the reclaiming or regeneration of rubber by P. Alexander.[1]

He first points out that soft rubber, containing comparatively low percentages of sulphur, alone comes under consideration here. In the case of hard rubber or ebonite (see next chapter), the finely powdered material, ebonite dust, can be used as such in mixings. If it is of high grade, the product is not essentially inferior to that made from mixings without dust.

The most remarkable feature in the whole question of regeneration is the truly extraordinary tenacity with which the combined sulphur is retained by vulcanised rubber. In consequence of this

[1] *Chemiker Zeitung; India Rubber Journal*, Oct. 1910, 421, 532, and 573.

the problem is confined to quite other objects than the production of a substance simulating raw rubber in all its properties. At the present time, in spite of the numerous claims, and the shoals of patents dealing with regeneration, this must be yet considered an unsolved problem.

Leaving this object then entirely out of consideration, Alexander defines Regenerated Rubber as "a product prepared from soft vulcanised waste rubber, which differs from the waste used in its production by containing a larger amount of rubber substance and by possessing greater plasticity." The latter is the typical characteristic.

Once this plasticity is imparted to the rubber it can be used with considerable freedom in many mixes.

The processes which aim at this result coincide in employing heat. This is sound, because plasticity is essentially a function of temperature. The best temperature is between the limits 150°—180° C., when heating is performed by liquids. Higher temperatures are employed when heating is performed on rollers. The changes in plasticity are closely connected with processes of polymerisation and depolymerisation. As was explained in Chapter II, this can also be expressed in terms of the degree of dispersion of the rubber colloid.

A very important question is the separation of the textile materials mixed with the waste rubber. The mineral fillers are not very objectionable so long as they do not interfere with the plasticity, since they are normal constituents of many mixes. This is not the case with textile materials. These can be removed by being blown away from the finely divided waste, which does not effect a very complete separation, or they can be destroyed by chemical means. For this purpose either acids or alkalies may be used. Alexander considers the use of the latter as decidedly preferable, since traces of acid exert a decomposing action on the rubber, while traces of alkali actually tend to preserve it.

In another type of process a reverse procedure is adopted. Instead of attempting to remove the fillers from the rubber, the rubber itself is dissolved by a suitable solvent, and the solution separated by decantation from the insoluble filling and textile

materials. The rubber is obtained from the solution by precipitation with alcohol or some similar liquid, or by distilling off the solvent. Theoretically the process is excellent, but Alexander considers it extremely doubtful whether any large amount of reclaimed rubber has been on the market which has been prepared by this process; the main objection is the high cost of organic solvents. This is a type of process of which many variations are possible, and a glance at the patent list frequently reveals a fresh modification.

Perhaps one of the best processes is one in which the solution of the vulcanised rubber is agitated with aqueous alkali at a high temperature in order to remove rubber substitutes (see later); the solutions are separated and the rubber obtained by distilling off the solvent. The rubber is then agitated with cold or slightly warm water.

However, in practically all the processes the main object is that of imparting plasticity. Beyond this there is often an attempt to "devulcanise" the rubber. Hitherto, as was said above, no definite proof has been adduced that it is possible to remove the combined sulphur, leaving a high class product. What can be done, beyond the restoration of plasticity, is to remove the free sulphur, by various sulphur solvents, which is of course quite another matter.

Analysis.

Shredded waste usually contains free sulphur. The amount should be determined, so that allowance can be made when deciding how much sulphur is to be added in the mix. The acetone extract should also be determined. This should not show great variations in a standard grade. The ash should be estimated, and a qualitative analysis made of it. (For methods of determination of free sulphur, etc., see Chapter VI). The amount of lead, lime, and magnesia may be important as affecting the velocity of vulcanisation (see p. 144). An estimation of rubber substitute, if present, may be advisable.

Reclaimed rubber on the contrary ought not to contain appreciable quantities of free sulphur, since this should have been removed in the process of regeneration. As mineral oils may

have been used in the process, the acetone extract should be examined for these bodies (see p. 130). Ash should be estimated, and a qualitative analysis made of it. The sample should be tested for acidity, since even traces of free acid might exercise a very deleterious action on a mixing made from such reclaimed rubber. This holds especially for rubber for electrical work. It is advisable to be somewhat conservative in using fresh sorts of reclaimed rubber, or at all events in making frequent changes. The utmost care should be taken to ensure that successive deliveries are as far as possible of the same composition. Weber[1] recommended an examination of the acetone extract for the presence of broken-down rubber, by just dissolving in a mixture of 2 volumes of benzene to 1 volume of absolute alcohol. On addition of slight excess of bromine a precipitate is obtained consisting of the bromine addition-products. This is washed with a mixture of benzene and alcohol, then with alcohol, and dried at 50° C. The bromine in this precipitate is estimated (method—see Chapter VI), and from the difference between the weight of the precipitate and the bromine in it the amount of decomposed rubber in the extract is obtained. In this way Weber obtained figures varying from 0·8 to 4 per cent. The method does not seem to have attracted much attention, but it appears worthy of a trial. It might be advisable to substitute carbon tetrachloride for benzene.[2] It is necessary to weigh the precipitate and also to estimate the bromine in it, since the bromine content will not be constant. The natural conclusion is that higher values, found in this way for rubber in the acetone extract, show that the treatment in the reclaiming process has been more severe.

Rubber Substitutes.[3]

These bodies (also called "factis") are mainly used for the purpose of replacing a certain amount of rubber by a cheaper material. At the same time they possess qualities which in themselves are useful for certain objects. The question is to

[1] "Chemistry of India Rubber."

[2] In this form the method is extensively used for the estimation of rubber in raw and vulcanised rubber, see pp. 63, 144.

[3] A useful monograph on substitutes is that of E. Seidl, in the *Jahrbuch der Kautschuk Industrie*, 1911, 75—198.

some extent a vexed one. It is easy to condemn their use hastily, but high authorities have pronounced in their favour under certain circumstances. It is probably safer not to employ them for the very highest classes of some kinds of work, but this still leaves open to them a wide field of utility. Good dark substitutes in particular have been recommended in small quantities for very high class mixings. According to Wächter, the use of substitutes should be exercised with caution in cable-making, which is perhaps one of the purposes requiring the most particular care. He more especially utters a warning against the use of substitutes of unknown composition. The necessity for caution in this direction is one which is well worthy of emphasis. It must not be understood that foolish conservatism is here advocated. On the contrary, it is most desirable that experiments should be made in mixing as in all other branches of manufacture. But it must be continually remembered that, when dealing with such a complex mixture as the average rubber mix, great care is necessary before introducing another constituent of comparatively unknown composition. In the first place, it is necessary to consider how far the proposed substitute is likely to be constant in composition. Further, when the composition is known, it is desirable to determine what action will take place between such a substance and the other components of the mix. This can be forecasted to a certain extent from theoretical considerations, which should then be verified by actual trial under various conditions. It will be seen that a number of important questions will arise in such a case; it is clearly of the greatest importance to settle these points, since neglect may lead to serious loss. Only the commoner well-known types of substitutes will be discussed here, but the rubber chemist may be called upon to investigate any of the almost innumerable substitutes which are being patented in such numbers—most of which are probably quite useless for the majority of purposes. Nevertheless, the chemist will require to examine them occasionally. Beyond the points above mentioned, it is desirable when dealing with a new substitute to ascertain its behaviour to the usual tests for rubber substitutes, and also to find, if necessary, other methods serving for its detection and estimation. For this purpose not only

should the substitute itself be examined, but a mix should be made, and the behaviour therein of the substitute considered, since it is very likely that it may be changed during vulcanisation by reacting with sulphur or from other causes, so that its solubility relationships and other properties may alter.

It is perhaps hardly necessary to emphasise that these substitutes do not really resemble rubber very closely. They cannot be said to replace it chemically. By themselves they do not exhibit the characteristics of rubber to any notable extent; these only appear after the addition to the mix of the requisite quantity of rubber. It is, of course, absurd to style them as "artificial rubbers"; synthetic rubber is the only sort which merits this description.

The majority of substitutes are prepared from fatty oils, usually by treatment with sulphur or sulphur chloride—a process superficially analogous to the vulcanisation of rubber. For this reason these oils are termed "vulcanisable oils." Chemically they are to be considered as derived from glycerol by replacement of the hydrogen atoms of alcoholic nature with fatty acid radicals. Such products are termed "glycerides"—"tri-glycerides" if three hydrogen atoms are replaced, as in the present case.

Glycerol. Three molecules stearic acid.

$$CH_2OH.CHOH.CH_2OH + 3\ C_{18}H_{37}.COOH.$$

give tristearin

$$CH_2O(C_{18}H_{37}.CO).CHO(C_{18}H_{37}.CO).CH_2O(C_{18}H_{37}.CO) + 3\ H_2O.$$

These tri-glycerides can be decomposed in the reverse direction, yielding glycerol and the corresponding acid. The process is termed "hydrolysis" or "saponification," and depends on the action of water. Under ordinary conditions water alone is too slow an agent, so that means must be employed to accelerate the reaction. This can be done by the action of acids, alkalies, or superheated steam. The latter method is of interest to rubber chemists, since one of the Admiralty tests prescribes the action of steam, under which conditions there is the possibility of hydrolysis of any rubber substitute which may be present. The same conditions are possible in practice, since various mixes must withstand steam, *e.g.*, when they are to be used for steam packings, etc.

From an analytical point of view the hydrolysis by alkalies is of interest, since it is by alcoholic solutions of alkali that the presence of rubber substitute in a mixing is detected. The alkali has the great advantage of forming a salt with the fatty acid which is liberated, and leaving the glycerol in solution, as in the manufacture of soap. Since the weight of fatty acid is an extremely large proportion of the total weight of glyceride (tristearin gives about 95 per cent. of its weight of stearic acid), it is possible to estimate the substitute not only by weighing the rubber before and after treatment with a hydrolysing agent, but also by isolating the fatty acid (which now contains sulphur) from the soap. This can be done by acidification and extraction with ether. Both processes will be described in detail later.

The substitutes formed by the action of sulphur on various fatty oils are known under the general name of "brown substitutes" or "dark substitutes." Formed by heating the oils with sulphur to about 150° C., they are dark brown masses of very slight elasticity. Their resemblance to rubber is by no means close. Beyond their use as bulking materials, they have been considered to possess value in preventing micro-porosity, in that they tend to fill up the microscopic pores of the mixing and thus render the mass more homogeneous. This may be put more definitely by saying that they tend to alter the degree of dispersion of the colloidal system, though their action is perhaps mainly in the direction of filling up minute air holes. In connection with this a test may be mentioned which was strongly recommended by Weber.

The substitute under examination is mixed in the required proportion with rubber on a small pair of mixing rollers, taking care not to overwork the rubber during the process. The mix thus obtained is examined under the microscope, when a good substitute will be found to be completely incorporated with the rubber, so that the mass appears perfectly homogeneous. With a bad substitute, on the contrary, mixing will appear incomplete and the two bodies will not seem to have blended properly. For this microscopical examination he recommends that the mix be placed on a

microscope slide, and moistened with a drop of benzene. A cover-glass should then be drawn across and left in position.

The products obtained by the action of sulphur chloride on fatty oils are called "white substitutes." Beyond these, the fatty oils can be oxidised ("blown") yielding other products which can be used in rubber mixes.

The chemical examination of substitutes should comprise a determination of total sulphur, chlorine, acetone extract, free sulphur and acidity. Details of the determinations will be found in Chapter VI, the methods being the same as those used for vulcanised rubber. The substitute should be finely crumbled for acetone extraction. Sulphur may be present in the acetone extract, not only in the free state, but also combined with oily matter. If it is desired to obtain a figure which only takes into account the sulphur present as such, the acetone extract may be treated successively with small quantities of acetone, 2 cub. centimetres at a time. The washings are poured through a small filter to retain the undissolved sulphur. This is then washed back into the original flask with a little redistilled carbon bisulphide (the crude solvent leaves a residue on evaporation). This is distilled off, and the free sulphur weighed. Owing to the solubility of sulphur in acetone, which though slight is appreciable, this method only yields approximate results.

With brown substitutes the total sulphur is frequently in the neighbourhood of 16 per cent. The free sulphur should be small. There is no need for a large amount, which only complicates vulcanisation, since less sulphur must be added to a mix to produce the same vulcanising effect. For this reason free sulphur should always be determined, and, if necessary, the quantity to be added to the mix should be diminished accordingly. The difference between the free sulphur and the total acetone extract mainly represents unchanged oil, which has not completely reacted with the sulphur during manufacture. The amount of the oily extract should be approximately constant in successive deliveries. The acetone extraction may be done as for raw rubber, except that five hours' extraction will usually be sufficiently accurate for

most purposes. The knowledge thus obtained of the amount of acetone extract is important when estimating the amount of substitute in a rubber mix, since allowance must be made for the substitute which passes into the acetone extract. The amount of matter soluble in acetone is liable to alter during vulcanisation: this point can be checked by the analysis of mixtures containing known amounts of substitute.

Acidity is estimated by boiling with alcohol (rendered just pink by caustic soda, using phenol-phthalein). In doing such a test, it is necessary to see that no trouble arises from the alkalinity which may result from the glass.

These substitutes can all be detected by their behaviour as tri-glycerides. They are soluble in alcoholic soda on boiling.

The distinction between brown, white, and blown oil substitutes is made by means of a chlorine and sulphur estimation. If chlorine is present in equivalent amount to sulphur, we are dealing with a white substitute. Brown substitutes contain sulphur, and no chlorine. Blown oil substitutes contain neither sulphur nor chlorine. Of course, mixtures of these may be present. The qualitative test for chlorine is that of heating with lime, dissolving in nitric acid, and testing with silver nitrate. The qualitative test for sulphur is that in which the substance is heated with sodium. After plunging the tube in water the solution is filtered, and a drop of a fresh-made solution of sodium nitroprusside added, when a purple colour is obtained.

Nothing more will be said about the various classes of substitutes, except to reiterate the necessity of careful examination:—

(1) For constancy in composition.

(2) For the possibility of estimating the amount present by the usual tests.

(3) For the manner in which the substitute will behave during vulcanisation. In this connection somewhat the same principle holds as that which actuates the pharmacist, when he compiles his tables of substances which are not "compatible" with one another. Thus brown

substitutes are chiefly used for hot-cured goods, but white substitutes for those in which cold cure is intended.

The Bitumen Group.

This group includes bitumen, tar, pitch, asphalt, and mineral rubber.

These bodies of a hydrocarbon nature are exceedingly difficult to characterise chemically. They may be residues from various kinds of distillation, such as petroleum; tar and stearine pitch are also used. Various kinds of bitumen also occur naturally, such as asphalt, Trinidad bitumen, and mineral rubber (M.R. is the usual contraction). The asphaltic substances are generally classed according to their solubility in successive organic solvents, such as petrol ether, carbon bisulphide, etc., which remove various fractions. In rubber work such an examination is not usually necessary.

These bodies are added mainly as filling materials, though they certainly have other uses, even if they do not always fulfil all the claims which have been made on their behalf. As softeners they enable mixing to be performed more readily. In the United States they are frequently used in conjunction with reclaimed rubber. One way of mixing is of interest. The M.R. is put on the rollers first, then the reclaimed rubber and the powders are added. The mix is cut out, and the raw rubber is masticated for a short time, after which the mix (still warm) is added. In this way it is claimed that the nerve of the raw rubber is preserved to the utmost extent possible. It has further been claimed that M.R. imparts increased durability to a rubber containing it. Within limits, this is very possible, since it will undoubtedly tend to diminish microporosity, with consequent liability to deterioration. Heinzerling and Pahl, in their researches on vulcanisation, found that asphalt exercised a beneficial effect on certain mixings.

Ash and total sulphur are to be estimated in these bodies, and also acetone extract, so that in a bituminous mix the increase in acetone extract from this cause can be allowed for. It may be further advisable to determine the amount insoluble in hot

pyridine. The direct estimation of these bodies in vulcanised rubber offers considerable difficulty. The solubility relationships of the different classes are very different, and when these are modified by possible combination with sulphur during vulcanisation,[1] it becomes almost impossible to solve the problem, especially since bitumen solvents are usually rubber solvents also (see p. 132).

Resins.

These fillers are used especially in the manufacture of ebonite. Among them may be mentioned ordinary resin or colophony (the residue from the distillation of turpentine), shellac and other hard resins. While colophony is fairly soluble in acetone, some of the hard resins are only soluble to a very small extent. These are soluble in dichlorhydrin ($CH_2Cl.CHOH.CH_2Cl$), B.P. 171°, or in epichlorhydrin. The former, with the higher boiling point, is the better solvent. They both tend to dissolve rubber. In this connection it is well to emphasise the fact, noted by Esch and Heil, that there is practically no organic liquid which is not capable of dissolving rubber at elevated temperatures, though this solubility may be very slight, and due to decomposition.

The main object of these fillers in ebonite is that of cheapness, as filling materials which do not leave any ash.

Waxes, Fats, etc.

Ceresin wax, consisting of the higher members of the paraffin hydrocarbon series, is largely used. It facilitates mixing in difficult cases and prevents sticking of the unvulcanised sheet.

Analytically, ceresin is soluble in acetone in the hot. It is very slightly soluble in alcohol on cooling.

Beyond taking the melting point, the acidity should be estimated. This ought not to be more than a trace. When the sample is boiled with neutralised alcohol and titrated with $\frac{N}{100}$ caustic (phenol-phthalein), 20 grammes should not require more than about 1 cub. centimetre, though this merely indicates the order of magnitude.

[1] Though mixes containing M.R. frequently contain very low percentages of sulphur, so that the M.R. will not alter much as far as solubility is concerned.

According to Weber, the presence of colophony as an adulterant may be detected by its solubility in 60 per cent. alcohol (cold) in which the ceresin is very slightly soluble. Allen (Commercial Organic Analysis) recommends 70 per cent. alcohol.

Other ingredients are beeswax (used in an ebonite mix called "Kiel compound"), camphor, palm oil, glycerine, resin oil and turpentine. In fact, at one time or another, there have been employed the most diverse ingredients. These are often added, usually on an empirical basis, for the purpose of remedying faults, such as porosity.

* * * * *

Before leaving organic filling materials it will be as well to remark that all dyes and fabrics which are to come in contact with rubber should be tested for acidity, and for copper or chromates, which can occasionally be detected in the ash. When this is the case the materials should be rejected, since they exert a very pronounced destructive action on rubber. They are considered to accelerate oxidation catalytically, though it is not unlikely that the action may be due to an acceleration of the oxidation of the free sulphur into sulphuric acid (see p. 87).

INORGANIC COMPOUNDING MATERIALS.

Sulphur.

Sulphur[1] occupies a unique position among compounding ingredients as the most effective vulcanising agent. The reaction between rubber and sulphur will be discussed at length in the next chapter, and at the moment it will be sufficient to describe some properties of sulphur itself.

Sulphur is well known to exist in various allotropic modifications. The stable modification at ordinary temperatures is the rhombic form, which consists of crystals in the rhombic system. Ordinary "flowers of sulphur" are composed of minute rhombic crystals. When heated to 114° C. rhombic sulphur melts to a thin yellow liquid, which becomes thick and viscous on further heating, at the same time assuming a much darker colour.

[1] There is a monograph on sulphur by E. Seidl, in the *Jahrbuch der Kautschuk Industrie*, 1909, 365—404.

Later, however, the liquid becomes thinner in consistency, and finally boils at 448° C.

There are other modifications which are more stable within various limits of temperature. Thus 93° C. is a transition point, above which rhombic sulphur tends to change into prismatic sulphur, which consists of crystals in the monoclinic system. These crystals are the stable form above 93°, and may be obtained by rapid cooling of molten sulphur. At ordinary temperatures they are unstable and slowly revert to the rhombic form.

When molten sulphur is cooled by pouring into water, a third variety, plastic sulphur, is obtained, which is probably a colloidal form. This also is unstable and reverts to the rhombic form at ordinary temperatures.

According to P. P. von Weimarn, when liquid sulphur, heated above 400° C., is poured into liquid air, threads are obtained about ½ to 1 millimetre thick. These are elastic and can be extended to about six times the original length. After a slight extension they return to their original length. After half an hour they turn into plastic form. They are a curious parallel to rubber, especially since they are probably in the colloidal state.

The so-called "insoluble" sulphur presents some difficult problems, which are scarcely fully elucidated yet, although valuable researches have been made by Küster, Alexander Smith, and H. Kruyt, among others. Küster showed that this modification of sulphur was very slightly soluble in carbon bisulphide, an excellent sulphur solvent. Although Budde has discussed the possibility of the occurrence of this modification in vulcanised rubber (where it may result possibly by the action of the steam, especially in cases where sulphuretted hydrogen can be evolved), the present author is of the opinion that the existence of this form of sulphur has not yet received the study which it demands. Weber certainly considered some such possibility when he was discussing the complete extraction of ebonite, which "contains the free sulphur in a peculiarly insoluble form—probably in an amorphous variety which only gradually passes into solution. This seems to be the reason why the substitution of carbon bisulphide for acetone proves no more expeditious, as the solubility of amorphous sulphur very largely depends on the temperature,

and would therefore take place much less rapidly at the boiling point of carbon bisulphide (46° C.) than at that of acetone (56° C.), although the latter is a much inferior solvent for sulphur than the former." Naturally, if such insoluble sulphur is present, it may vitiate estimations of free sulphur in vulcanised rubber, since it is unlikely that simple extraction with a solvent will remove such sulphur in any reasonable time, for the researches quoted above show that the solubility of this modification is slight, and its amount is actually estimated by extracting sulphur containing it, with carbon bisulphide, though only for short periods. Consequently, research is required to determine the extent of the occurrence of this body in vulcanised rubber. Hinrichsen has made some observations on the subject, and has shown that it can occur in cold-cured rubber, formed by the action of moisture on the sulphur chloride. In this case he was able to show that a sample, extracted with sulphur solvents, lost a further quantity of sulphur by treatment with yellow ammonium sulphide, followed by very careful washing with water, alcohol and ether. This showed clearly that insoluble sulphur had been present, and was removed by ammonium sulphide.[1]

For the purposes of vulcanisation it might be considered at first that it is immaterial which modification of sulphur is employed, since the operation is conducted above the melting point of sulphur. However, recent researches lead to the conclusion that differences can persist even in the liquid form. This is borne out to some extent by actual practice, since it is considered that different qualities of sulphur do not always yield the same results on vulcanisation. This point had been considered by Weber before the researches of Kruyt had appeared.

Sulphur is most usually employed in the form of flowers. These are tested for acidity, moisture, and ash. According to Weber, acidity is estimated by taking 5 grammes of sulphur, moistening with alcohol (so that the powder will wet), adding water and titrating with $\frac{N}{10}$ *NaOH*. The acidity should be no more than just perceptible, for the reasons given above. Seidl recommends

[1] For a more detailed discussion of the researches of Alexander Smith and others, see *The Rubber World*, 7th Sept., 1911, *et seq.*

making 10 grammes into a thick paste with water and testing with blue litmus, stating that sulphur should be absolutely acid-free.

Ash is determined on a large quantity, as it should be negligible in amount.

Weber pointed out that moisture ought not to be estimated by drying in an oven. The best way is to dry in an exsiccator in vacuo, over sulphuric acid. The drying is done to constant weight, which does not require an unreasonable time. Sulphur should be dry, especially for ebonite.

The atmospheric oxidation of sulphur has been studied by Gardner and Hodgson,[1] who found that, on heating 1 gramme at 100° C. for 102 hours, 0·3 per cent. was converted into acid. In presence of copper sulphate this amount increased to 1·48 per cent. As mentioned above, this may explain the profound destructive action of traces of copper on rubber. They also note that the rate of oxidation increased with the fineness of division of the sulphur.

Determination of the actual percentage of sulphur present in flowers of sulphur is rarely necessary. The commercial product is of exceedingly good quality. The determination is not so simple as might appear at first sight. Sulphur is practically always estimated by conversion into sulphuric acid, which is usually weighed as barium sulphate. The oxidation is generally performed by fuming nitric acid. If it is carried out in an open vessel, the results tend to be too low, owing to loss of SO_2 or possibly loss by extremely fine spraying. If, on the other hand, the oxidation is performed by the Carius method of heating in a sealed tube with nitric acid, the results are liable to be high. Anelli, who has recently investigated this part of the subject, recommends adding barium chloride to the contents of the tube before heating. In this way, as Rupp has also pointed out, a very dense precipitate of barium sulphate is formed which can be readily washed, and Anelli also claims that a too high result is avoided (due to silica from the glass). The experiments of the present author show that the oxidation in open vessels is a very delicate operation indeed. This will be discussed further in Chapter VI.

[1] *Journ. Soc. Chem. Ind.*, 1910, 672.

Sulphur Chloride.[1]

This compound (S_2Cl_2), though not a compounding ingredient, will be discussed here as a vulcanising agent.

It is prepared from carbon bisulphide by the action of chlorine, in presence of iodine as chlorine-carrier. It is a reddish brown liquid (sp. gr. 1·68, B.P. 135° C.). It is soluble in benzine, benzene, carbon bisulphide, carbon tetrachloride, etc. In contact with water it is decomposed, giving insoluble sulphur and hydrochloric acid. The commercial product may contain dissolved sulphur, or sulphur dichloride SCl_2. The latter impurity is objectionable.

The action of sulphur chloride on rubber will be discussed in the next chapter, where a method will be found by which the chlorine may be estimated.

Details of the analysis of sulphur chloride as recommended by Fawsitt may be found in his paper in *Journ. Soc. Chem. Ind.*, 1886, p. 638.

Golden Sulphide.

Antimony sulphide (Golden or Crimson Sulphide) is usually classed as a vulcanising agent, though its action is due to the free sulphur which it contains, often in very considerable amount. It is prepared by the action of acid on a soluble thio-antimonate, and may then be further purified. The thio-antimonate is prepared from antimony trisulphide by the action of alkali and sulphur. The pentasulphide results thus :—

$$2\ Na_3SbS_4 + 3\ H_2SO_4 = 3\ Na_2SO_4 + 3\ H_2S + Sb_2S_5.$$

Since calcium salts are often used, the product frequently contains notable amounts of calcium sulphate, as well as an excess of sulphur. The various colours, ranging from crimson to golden, are obtained by using different strengths of acid in the decomposition of the thioantimonate.

Antimony sulphide is added to rubber mixes not only as a vulcaniser, but especially on account of its tinctorial powers, in the manufacture of red rubber goods.

The sulphide can be tested for acidity, covering power,

[1] The monograph of Seidl, already mentioned, may be consulted for detail.

stability of colour, free sulphur, total sulphur, antimony, mineral impurities, etc.

The sample is examined for **acidity** in the aqueous extract. Sulphuric acid may be present. This should be tested.

Covering power is measured in the manner recommended by Weber for white lead, etc. In this case equal small quantities of the sample and of a standard are mixed with the same amount of linseed oil and standard white lead (though any white lead will suffice). The two samples are well worked into the white lead and the two mixtures are compared side by side, when small differences in colour may be readily detected.

Stability against temperature, etc., may be measured by heating to 280° F., or better by mixing a small quantity with rubber in standard proportions and vulcanising (Ditmar).

The estimation of **free sulphur** is of the greatest importance, since on this depends the vulcanising efficiency. Weber recommended a method with ammonia, on the ground that warm carbon bisulphide decomposed the pentasulphide.

However, Lederer[1] remarks that it has been shown that this is not the case for pure bisulphide. Since pure carbon bisulphide decomposes with time, he recommends using ordinary "pure" carbon bisulphide in a soxhlet, when only the pure condensed vapour comes in contact with the sample. A known amount of the solvent must be used, and the same amount must be distilled down in a weighed flask to find the correction for impurities in the solvent. Extraction should be continued for ten hours. On this result will depend the amount of sulphur which is to be added to a mixing.containing antimony sulphide. Obviously, the lower the free sulphur, the more sulphur must be added, to bring the available free sulphur up to a fixed amount for that particular mixing.

Total sulphur is estimated by oxidation with nitric acid. To avoid violent action treatment with dilute acid is advisable first. After evaporation on the water-bath, conc. acid (sp. gr. 1·4) may be used, finally treating with fuming acid. The following further treatment is advisable. After evaporation to dryness

[1] In an article on Antimony Sulphide. *Jahrbuch der Kautschuk Industrie*, 1910, 93—102.

with 1 (or 2) grammes potassium nitrate, addition of 5 cub. centimetres dilute *HCl*, 4 (or 8) grammes potassium chloride and water, the liquid is filtered, and precipitated with barium chloride. (For details of precipitation see p. 126.) If filtration is difficult, tartaric acid may be added to bring the antimony into solution. A blue-band "589" Schleicher and Schüll paper is useful here, since this paper will retain very fine precipitates.

Antimony is usually determined as the tetroxide, Sb_2O_4. Lederer recommends treatment on the water-bath with hydrochloric acid, adding nitric acid to oxidise the sulphur, evaporation, and filtration from the residue, after taking up with *HCl*. Silica and calcium sulphate may be determined in the residue. Antimony is precipitated in the filtrate with sulphuretted hydrogen and weighed as Sb_2O_4. Details of this manipulation will be found in the estimation of antimony in rubber goods (Chapter VI).

Other Mineral Fillers.

The other mineral fillers, though of great importance, do not call for the same detailed consideration. They have specific purposes, which frequently depend rather on physical than on chemical grounds. They are all to be tested for moisture, and for acidity where this is likely to be present. Further, a qualitative analysis should be carefully made, so that the supply is always up to the standard. A few of the more important of these fillers are:—

Lead Compounds.[1]

Litharge and lead thiosulphate accelerate vulcanisation; the mechanism of this action will be considered in Chapter V. Articles containing these bodies are practically always dark coloured, owing to the formation of black lead sulphide.

White lead is used in cold-cured goods as a pigment. Red lead is a hardening agent.

Magnesium Compounds.

French chalk (a silicate of magnesium) is a very common filler, which is also largely used as an imbedding material for curing. Beyond estimation of moisture, it is useful to determine the loss of weight on ignition. This may amount to about 5 per

[1] See *Jahrbuch der Kautschuk Industrie*, 1910, 103—111, Seidl.

cent., and a correction to this extent may then be made when the ash is determined on a sample of a mixing containing French chalk. In this way the amount of French chalk originally added may be determined; without such a correction the result is too low.

Magnesia is used in the form of carbonate, and of oxide (magnesia usta or calcined magnesia). Both are to be obtained in dense and in light powers, "heavy" and "light." The specific gravity may be determined by placing in a graduated cylinder (empty) and adding a known volume of alcohol, when the volume of a known weight of the magnesia can be determined. Esch recommends a determination of the degree of fineness of the powder by placing in a graduated cylinder, tapping this on the bench (best a specified number of times) and reading the volume of the dry powder. This test may also be performed with other mineral fillers. In every case comparison is made with previous data obtained with the same substance in former consignments.

Carbon dioxide can be estimated in magnesium carbonate in the Schrötter apparatus, by the loss of weight on treatment with acid.

Calcined magnesia[1] is useful, not only to neutralise traces of acid, but above all as an accelerator of vulcanisation, particularly for resinous rubbers. There has been considerable controversy as to whether the light or the heavy variety is preferable. The light is dearer weight for weight, but it goes farther on account of its low specific gravity. It may cause porosity, by incorporating air with the mixings on account of its lightness. Both are extensively used, and, as Esch remarks, it is possibly a matter of taste as to which is preferred.

Calcium Compounds.

Lime is used as an accelerator of vulcanisation: both air-slaked lime and quicklime are effective. Although the latter is rather apt to cake, it is recommended as an astringent for soft tacky rubbers. As these are difficult to dry, it also binds traces of moisture. Weber[2] gives a useful method of detecting lime in

[1] See *Jahrbuch der Kautschuk Industrie*, 1910, 77—92, K. Miksch.

[2] "Chemistry of India Rubber."

vulcanised rubber in presence of calcium carbonate, by dissolving out with a solution of sugar.

Whiting (calcium carbonate) is largely used as a filler, especially in the States.

Zinc Compounds.[1]

Zinc oxide is a particularly valuable filler, which imparts very useful properties to a mixing. It is, however, too expensive for many purposes, though it is largely used for white mixes. It is tested for traces of sulphates and for lead and iron, which injure the colour. Zinc may be estimated by titration of the hot hydrochloric acid solution with potassium ferrocyanide, using uranium acetate as an external indicator. The end-point is reached when a brown coloration is just obtained after the lapse of a definite time, say one minute. A blank is done with the same amount of hydrochloric acid and the same volume of solution, so that allowance can be made for the ferrocyanide required to give the end-reaction. The ferrocyanide is standardised against pure zinc.

Other zinc compounds are zinc sulphide and lithophone (containing zinc sulphide and barium sulphate). Both are pigments.

Carbon Black is tested for covering power, for dyes (by boiling in spirit) and for oils by acetone extraction (Weber).

Among other fillers which require no detailed description are barium sulphate (which, curiously enough, is regarded as quite a general filler among some of those unacquainted with the subject), silica, vermilion (*HgS*), china clay, asbestos, silica, etc. Here again the number of possible bodies which may be added to rubber mixings is very large.

LITERATURE.

Works which may be consulted are:—"Crude Rubber and Compounding Ingredients," by H. C. Pearson; "Chemistry of India Rubber," by Weber; and the monographs in the German *Jahrbucher der Kautschuk Industrie*, to which individual reference has been made. Examples of actual mixings will be found in "The Manufacture of Rubber Goods," by Esch and Heil, and "Die Fabrikation der Gummi-drähte Kabel," by M. Wächter.

[1] *Jahrbuch der Kautschuk Industrie*, 1911, 99—107, Lederer, may be consulted for detail.

CHAPTER V

VULCANISATION

ALTHOUGH rubber was employed in manufacture before the discovery of vulcanisation, this fundamentally important invention gave a great impetus to its use.

Goodyear, of Connecticut, has the honour of priority. In the year 1839 he succeeded in obviating the disadvantages attaching to the use of raw rubber for shoes and other purposes, by heating with sulphur. He did not patent the process. A portion of the product was shown to Thomas Hancock, who at once perceived its technical value. This stimulated him to continue a laborious series of experiments, in which he endeavoured to produce what he termed "the change" in rubber. After a most strenuous and patient period of experimentation, treating the rubber under all manner of conditions with and without sulphur, he at last succeeded—as it seemed, almost by accident. He discovered that rubber dipped in a bath of molten sulphur exhibited the long sought "change." This was one of the accidents which are the result of such toilful search that the result was almost bound to be obtained sooner or later. It must be admitted that the discovery throws more credit on Hancock's patience than on his scientific method. For instance, he states that he never analysed the product which he was attempting to reproduce. Nevertheless he succeeded at last, and in 1843 took out an English patent for the vulcanisation of rubber by dipping in a bath of molten sulphur

In 1844 Goodyear patented his method, which consisted in heating a mixture of rubber and sulphur.

The patent of Parkes, for cold vulcanisation by the use of sulphur chloride, appeared in 1846. Thus in the space of seven years the three chief methods of vulcanisation became known. It is most remarkable that to this day, in spite of the many patents on the subject, these methods still hold front rank, with the same essential details.

At the same time it must be remembered that the most

important of the three, that of Goodyear, relates to a general principle, of which the possible variations are almost infinite. Much remains to be done in the direction of securing greater control of the process which can only be effected by a profound knowledge of the nature of raw rubber itself, and also by a more intimate acquaintance with the mechanism of the reaction of vulcanisation.

A few of the early discoveries following the three great ones may be noticed.

1846. Use of moulds in curing (Hancock).

1848. Manufacture of hollow rubber goods (Goodyear).

1851. Discovery of Ebonite (Goodyear).

At present the chief methods of vulcanising or "curing" are as follows :—

(1) Dipping in molten sulphur.

(2) Heating with sulphur, with and without carriers of sulphur, such as lead compounds, etc.

(*a*) Heating the mixture in hot air.

(*b*) Heating in steam.

In these cases the article may be heated direct, or placed in a mould. It may be wrapped in cloth, or metal foil, or embedded in French chalk. It may even be heated beneath water. In short, any method may be tried whereby a mixture of rubber, sulphur, and other substances is heated above about 247° F. The results by various of these methods are not the same in actual practice, and the choice of a particular one is by no means a matter of indifference.

(*c*) The mixture may be heated in a press (steam-heated iron plates).

(3) Cold curing, either by dipping into a solution of sulphur chloride in carbon bisulphide or other solvent, or exposing to the vapour of sulphur chloride, or, according to the recent patent of Bloch, by dipping into a solution of hydrogen persulphide.

(4) Less used methods.

(*a*) Heating under pressure in a bath of an aqueous solution of calcium polysulphide.

(*b*) Heating with antimony iodide and sulphur. This was devised by Fawsitt, to accelerate the ordinary process.

(*c*) Heating with metallic sulphides. This is essentially a variation on (2), for the vulcanisation is due to the free sulphur contained in, or produced from, the sulphide used.

(*d*) The acidising process, which is quite different from any of those which have been mentioned, as it consists in treatment with hypochlorites.

With the unimportant exception of the acidising process, it will be seen that vulcanisation consists in the union of rubber with sulphur or sulphur chloride.

It is unnecessary to dwell for long on the manifest advantages which result from vulcanisation. For technical purposes it effects the changes which transform a raw product of uncertain applicability into a finished and valuable article, with properties which within certain very wide limits can be made exactly to the requirements of the user. Thus vulcanised rubber as compared with raw rubber is less sensitive to changes of temperature, neither sticking to itself when warmed, nor becoming hard so soon under the influence of cold: it is mechanically superior in elasticity and tensile strength: it is more durable and more resistant both to chemical and other agents. Further, by varying the amount of sulphur, these valuable properties can be progressively altered in almost any desired direction. Thus the hardness may be increased till ebonite is reached; starting from the softest of rubbers, with the lowest sulphur content, the increase of hardness occurs gradually with the rise in sulphur content till ebonite is reached, first cheese-like in consistency and finally very brittle. In fact the reaction is so valuable in scope that it can be compared on most favourable terms with that between iron and carbon, which offers such bewildering possibilities in the production of steels.

The theoretical principles underlying the reaction are of great importance, because it is clear that, with such an infinite number of possible combinations, much time, labour, and expense will be spared when calculation can replace the method, which is unfortunately not rare in technology, whereby a combination is made of

a traditional knowledge of existing mixings and processes, and a series of empirical attempts at improvement, which are little more than shots in the dark.

It is first necessary to draw a picture of the quantitative relationships which exist, in so far as the experimental material is at hand. This is difficult on account of the complexities of the problem. The number of variables is so great that the most carefully devised plan of research is necessary in order to obtain figures at all comparable with themselves or with the figures of other workers. It is to be regretted that hitherto sufficient precautions have not been taken in this respect. This applies to the two most comprehensive series of experiments on the subject, with the exception of those of Weber. Thus Heinzerling and Pahl conducted a most laborious examination of the effects produced in compounded rubber by the addition of various substances. The idea was excellent, but the execution suffers from the defect that too many mixings were taken, in none of which were the conditions really closely studied. From the method of experiment, the results are not strictly comparable, and, as Weber observes, the mixings used represent "weird specimens of the rubber mixer's fancy." As the result, it is unfortunate that these tables, giving both chemical and physical tests on these different mixes, are not of nearly the value which might be expected from the amount of labour spent on them. These tables occur regularly in almost all the books, and may be consulted there. They will not be quoted here in any detail.

Again, exhaustive studies on vulcanisation have been carried out by Ditmar. Without denying the value of these researches, it must be recognised that although the general plan of the work was carefully devised, the experiments suffer from the defect that the mixings were made on a very small scale, and that the samples were vulcanised under conditions which were not very likely to occur in practice. On this account they have been subjected to considerable criticism.

These two series of researches were of a complicated nature: at the moment it is necessary to consider experiments on a simpler basis, together with a number of fairly generally accepted facts. The following points seem clearly established:—

(1) The reaction is an addition and not a substitution. In other words, the sulphur or sulphur chloride adds at the double bonds, instead of replacing an equivalent quantity of hydrogen. This was conclusively demonstrated by Weber, who lavished an amount of energy on the proof of this statement which is now scarcely necessary to give at length, though at the time it was highly requisite, on account of the extraordinary views on the nature of the reaction which were current.

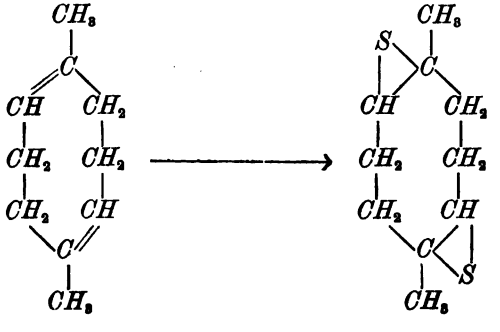
If the reaction were a substitution, the following equation might represent it:—

$$C_{10}H_{16} + S_2 = C_{10}H_{14}S + H_2S.$$

If the hydrogen of the rubber is replaced by sulphur in some such manner as this, it is clear that a very large amount of sulphuretted hydrogen must be evolved in the process. On the basis of the above equation, about 2,000 gallons of the gas would be evolved per ton of rubber vulcanised to ebonite. Although in this case a small amount of the gas can be detected, it is not due to the normal reaction, but is produced either from the impurities always present, such as protein or resins, or from a substitution reaction which may occur under the influence of excessive heat. Indeed, Weber found that such an abnormality occurred in the case of an ebonite which had been cured to a very high extent. However, in normal cases, Weber showed that sulphuretted hydrogen was not produced to any appreciable extent, and that accordingly the reaction was additive:—

$$C_{10}H_{16} + S_2 = C_{10}H_{16}S_2.$$

This is explicable if rubber possesses two double bonds. Taking the constitutional formula ascribed to rubber by Harries we have:—



It will be understood that the above formula refers to the formation of hard rubber, or ebonite. In the case of soft rubber, the amount of sulphur which enters into combination is much smaller. The maximum amount of sulphur contained in normal samples of ebonite is, according to Weber, 32·6 per cent., which corresponds to the above formula. This can scarcely be regarded as absolutely proved from an experimental point of view.

In the case of cold vulcanisation a similar reaction occurs with sulphur chloride, except that, according to the recent work of Hinrichsen and his co-workers, the maximum corresponds to the formula $(C_{10}H_{16})_2S_2Cl_2$. It had been stated by Weber that double this amount of the chloride could be taken up, but it appears from the later work that this result was probably an accidental one, since it was observed that most variable results were obtained by Weber's method of experiment, and it was only possible to secure constancy by the use of an indirect method, which will be mentioned later.

(2) The amount of sulphur which combines with the rubber in this manner depends on many variables, but under the same conditions it is proportional to the time of heating and to the amount of sulphur originally added. The extent of vulcanisation depends on the amount of sulphur added, and, as already said, this can yield anything from soft rubber to ebonite. It is desirable to have some numerical measure of vulcanisation. This is attained to a certain extent by a figure called the "coefficient of vulcanisation," which represents the extent to which the above addition reaction between rubber and sulphur has occurred. In the case of ebonite the product is assumed to possess the structure shown by the formula. Soft rubber was considered by Weber to represent a mixture of various members of a series comprising at least ten sulphides of rubber, ranging from

$$(C_{10}H_{16}S_2)_{10} \text{ to } (C_{10}H_{16})_{10}S_2.$$

The experimental base of this conclusion cannot be regarded as in any way convincing, and we shall see that there are other ways of considering the matter.

The "coefficient of vulcanisation" was introduced by Weber. It

is obtained in this way:—Calling the amount of sulphur present the "total" sulphur, the amount combined with the rubber the "combined,"[1] and that uncombined the "free"—the combined sulphur is called the "sulphur of vulcanisation," and the ratio of this last to the amount of rubber actually present is the required coefficient. Thus in a mix containing 50 per cent. rubber, with 3 per cent. sulphur, of which 2 per cent. is combined, the coefficient is clearly 4 per cent. Soft rubber may be considered to be cured with a coefficient as low as $2\frac{1}{2}$ per cent., while in ebonite the coefficient may be as large as 50 per cent.

The importance of some such numerical expression of the extent of cure is obvious. It is extremely unsatisfactory to leave the question to the mere description of the manipulator, especially for purposes of future reference. It is unfortunate that the coefficient of vulcanisation, though it offers valuable assistance, is in itself a variable magnitude, in that rubbers with the same coefficient may possessvery different properties. This was ably discussed by Weber, who pointed out that the process of vulcanisation really consisted of two parts, or rather depended on two factors:—

(*a*) The physical condition of the rubber colloid.

(*b*) The pectisation [= coagulation] of this colloid by the action of the sulphur or sulphur chloride.

As he remarked, (*a*) is a factor of the utmost variability. Not only does it depend on the botanical origin of the rubber, on its geographical source, on the method of coagulation adopted and on a host of other variables, but it also depends on the treatment which has been undergone by the rubber in the works. Beyond this, owing to the high temperatures of vulcanisation (compared with the temperature to which the unvulcanised material can be submitted) changes in physical condition will be occurring during the process itself. For the moment we are rather concerned with (*b*), which is a process of comparatively much greater

[1] This refers to mixes in which no sulphur is contained in the fillers. If these contain sulphur, it is necessary to distinguish between "combined sulphur," *i.e.*, sulphur not present in a free state, and sulphur combined with the rubber itself, *i.e.*, sulphur of vulcanisation.

definiteness. In fact, Weber stated that as a chemical reaction the vulcanisation process is not influenced by the physical state of the rubber colloid, but that the state of the rubber colloid while under vulcanisation largely determined the physical constants of the vulcanised product. Thus the same coefficient of vulcanisation by no means indicates that the same physical properties will be found. Even with the same batch of the same mix, a sample cured at 290° F. will not possess the same properties as one cured to the same extent (chemically) at 280° F.

Although this may have to be modified slightly by the work of Axelrod, and by more modern theoretical considerations, there is much truth in it, and we can accept his conclusion that the action of sulphur consists very largely in a pectisation of the rubber colloid (*i.e.*, a coagulation), or, as he puts it, a fixation by sulphur, which perpetuates the physical state of the rubber which prevails at the time.

Researches have been carried out by Weber, Stern, Hübener, and Bysow on the quantitative aspects of the process of vulcanisation, considered as far as possible apart from the varying physical states of the rubber. They find that, as practice would indicate, the combined sulphur increases with the amount of sulphur present, the time of cure and the temperature employed. The connection between the velocity and the amount of sulphur appears to be of an exponential character, *i.e.*, the velocity varies as the xth power of the concentration of sulphur (see p. 104).

Concerning the physical condition of the rubber colloid, it is found that the speed of vulcanisation varies with the nature of the raw rubber. Weber conducted experiments which led to the conclusion that at 125° C. Para vulcanised on the whole somewhat faster than Borneo or Upper Congo, rather slower than Ceara, and considerably slower than Beni River. At 135° C. Para vulcanised almost as fast as Beni River, rather faster than Upper Congo, and considerably faster than Ceara and Borneo. These results cannot be regarded as absolutely characteristic for these brands, for there are many variables to be taken into consideration besides the source. This may be seen especially in the case of plantation rubber, where one of the objections made to its use is that the vulcanisation is apt to be irregular (see p. 31). As great

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variations exist between the latex yielded by even neighbouring trees, it is quite likely that such variations may be the cause of differences in the vulcanising capacity. The method of coagulation introduces further variations, as may be seen from the work on Kickxia latex by Marckwald and Frank, who showed that very different results were obtained in quality and in vulcanising capacity when coagulation was effected by various processes. In comparing the speed at which very resinous rubbers vulcanise in practice, when a great excess of sulphur may not be present, it must be remembered that the action between resin and sulphur may remove a portion of the sulphur, and thus reduce the apparent velocity of vulcanisation.

Weber's views threw a flood of light on the subject of vulcanisation, and his idea as to the perpetuation of the then prevailing physical state of the rubber by an addition reaction with sulphur was most illuminating. With the reservation as to the change in the physical state of the rubber during the vulcanisation itself, which, indeed, was indicated by Weber himself, this much appears irrefutable at the present time. His views on the existence of a series of chemical compounds between rubber and sulphur must now be regarded with doubt. At the moment there is a distinct tendency in certain quarters to revert to earlier theories in a modified form. At the time when these theories were current they were scouted as unscientific, by Weber in particular, but they now appear to have contained much truth, even though they were expressed with some lack of scientific precision.

* * * * *

The most recent step in this direction has been taken by Wolfgang Ostwald, who has considered the whole question of the taking-up of sulphur during vulcanisation from a physico-chemical standpoint. He points out that there are various facts which have not received a satisfactory explanation on the orthodox chemical theory. Some of these points were raised before by industrial chemists, but their views did not find general acceptance, with the result that at the present the physical theories are considered to possess merely historical interest. Ostwald suggests that sulphur is taken up in vulcanisation by a process of adsorption. Before discussing his exposition of this theory some

account may be given of the phenomena of adsorption in general, and the remarkable parallelism which exists between the processes of vulcanisation, dyeing, and tanning.

In these cases we also find that colloidal substances undergo a certain reaction, by which another substance is fixed on them in such a way that their properties are profoundly modified. Thus in dyeing a fabric there is a very great resemblance to the vulcanisation of rubber. The fabric is a complex organic colloid, which, on account of its chemical structure, may possess the power of reacting with the dye, in the same manner that rubber can react with sulphur on account of its unsaturated nature. Wool and silk are proteins, and the molecule contains both basic NH_2 groups, and acidic $COOH$ groups. The molecule thus possesses simultaneous basic and acidic capacities, and as dyestuffs are of an acidic or basic character, there is the possibility of salt-formation between dye and fibre. This is the chemical theory of dyeing, which is a simple and useful attempt to explain the observed phenomena. At the same time, its very simplicity is against it, and there is much to be said in favour of a more physical view of the matter. The most obvious explanation in this direction is that which regards dyeing as a process of simple absorption of dye by fibre, in the same way that dyesalts are absorbed or dissolved by water. It is found that this theory, due to O. N. Witt, is untenable, because when the concentration of the dyebath is varied, the amount of dye taken up by the fibre does not vary to the extent demanded by the theory.

The most modern, as it appears the most satisfactory, way of considering the process is to regard it as an adsorption process. It is first necessary to consider a simple case of adsorption.

When a solution is in contact with air, with a solid, or with another liquid (with which it does not mix), a tendency may exist by virtue of which the dissolved substance will become more concentrated at the boundary or surface of separation. Taking a concrete example, in which for simplicity two liquids are involved, a drop of oil suspended in a solution of soap and water may be considered. Around the drop there will be a layer of soap solution, which is much stronger than the bulk of the solution. The strength will rapidly diminish as the distance from the drop

increases, till the strength of the bulk of the liquid is reached. This layer of concentrated solution will be excessively thin, but it can exert an important influence, which recalls the action of protective colloids in the latex. If the oil is present in a high state of dispersion as an emulsion, it will be found that little or no oil is removed by shaking with ether, which is normally an excellent oil solvent. Presumably this is because the film of adsorbed soap or soap solution prevents contact between oil and ether. After coagulating the emulsion by the addition of acids (or faster by alum), the oil is once more soluble in ether. The globules have united, the surface has lessened enormously, and the amount of soap adsorbed is now negligible. The protecting film can now be broken: the oil is thus soluble. The analogy with the protective action of colloids is close—indeed, it is not certain that the soap does not act in this way.

It has been shown by J. Willard Gibbs, in his classical work on thermodynamics, that only those substances which lower the surface tension between oil and water can be adsorbed by oil. Soap does this, as can readily be seen by the behaviour of a thin stream of oil in a soap solution. Whereas in pure water the oil will form large drops, in a strong soap solution the oil will either form very small drops, or run in a continuous stream. Evidently then soap lowers the surface tension between oil and water. It follows on theoretical grounds that soap must be adsorbed by oil.

In passing, it may be noted that this conception sheds much light on the theory of the detergent action of soap. F. G. Donnan and the author have shown that the power of emulsification of a soap varies with the effect of that soap on the surface tension. It is evident that the washing effect is closely connected with the emulsification of the oil of the skin by the soap solution.

An effect similar to that of the oil globules in soap solution can be observed in a manner much more visible to the eye, with sand or charcoal, and the solution of a dye in water. If a red solution of the dye Congo Red in water is poured through a thick layer of fine sand, this will be stained a deep red, and the liquid will pass through colourless at first. The dye has been adsorbed or

concentrated upon the surface of the grains of sand. It must be emphasised that the effect is purely superficial: it concerns the surfaces only. The dye is held *round* the grains of sand, and is not dissolved *in* the sand or chemically combined *with* it.

A more complex but more suggestive case is the dyeing of wool by Congo Red. As a colloid, the wool possesses an enormous surface, and over this surface a concentration of dye may occur, that is, an adsorption. It has been shown theoretically, and verified practically, that the adsorption from a weak solution is proportionately much greater than from a strong solution. Although the amount adsorbed from a 1 per cent. solution will be greater than that adsorbed from a 0·1 per cent. solution in normal cases, yet it will not be ten times as great. The investigations of Freundlich have shown that this can be expressed as follows for many varied types of dyeing :—

Concentration of dye in the fibre = constant × (final concentration of the bath)$^{\frac{1}{n}}$.

This will be seen to be merely a mathematical statement embodying the above conclusion. He found that the values of n were fairly constant whether charcoal was used or whether the more complicated case of dyeing on wool, cotton or silk was examined. As the result of his work he arrived at the conclusion that dyeing was clearly a case of adsorption. Subsequent work by Freundlich and others has shown that this view may require enlargement in various directions. Something will be said about this insufficiency when discussing Ostwald's views on vulcanisation.

With an ordinary piece of filter paper adsorption effects can be observed, which play a very great part in the washing of precipitates. This would be a much more rapid process if adsorption of the dissolved substance by the paper did not exert a retarding influence. An excellent example of this adsorption may be observed when a drop of dyestuff solution, such as Congo Red, is allowed to fall on filter paper. A red zone will be produced at the centre, and a colourless zone of water will be found surrounding this. The filter paper has adsorbed the dye, and beyond a certain point only water spreads. If a mixture of

two dyes is used, the adsorption may be preferential, so that a zone of red may appear in the centre, surrounded successively by zones of blue dye and colourless water.

A final and striking example may be given, which is of importance. It is well known that animal charcoal possesses the power of decolourising solutions. This is again a case of adsorption of the colouring matter. The animal charcoal possesses a very great surface, being of a colloidal nature, so that it can hold a large amount of a dye, for example. When it is shaken with a solution of methyl violet, the charcoal is "dyed" and the solution is partially or wholly decolourised. In this case chemical combination appears unlikely, yet when the charcoal is taken from the solution the dye is not removed by simple shaking with water, in which normally it dissolves. In the case of most dyes, however, water will remove them from the charcoal on which they have been adsorbed.[1]

It will be seen that adsorption is a very general phenomenon; it is especially characteristic for colloids, on account of their great surface, due to the mesh-like or similar structure.

* * * * *

In outlining his theory, Wo. Ostwald notes that, as in the theory of dyeing, the earlier explanations of vulcanisation were on the whole of a more physical nature. The exponents of these views expressed them in a somewhat vague manner, so that the greater definiteness of the chemical explanation secured a considerable amount of support for it, with the result that modern writers have tended to dismiss the physical theories very hastily.

The main points brought forward by Ostwald are these:—

(1) That the reaction between rubber and sulphur is purely additive in character: substitution of hydrogen by sulphur does not occur. While this does not show that the process is one of adsorption, it opens the door to such an explanation, since it renders possible the conception that the sulphur is taken up by a process which does not necessarily involve any breaking of the molecule.

[1] Recent experiments show that very highly purified charcoal does not behave in the same way; it is possible that the rigorous purification has coagulated the colloid, however.

(2) It is well known that a continuous series of these addition products of rubber and sulphur exists. The proportion of sulphur may be varied at will, with resulting variation in the properties of the product. This gradation is highly characteristic of adsorption processes. Weber attempted to explain it by the existence of ten sulphides with regularly increasing sulphur content from $(C_{10}H_{16})_{10}S_2$ to $C_{10}H_{16}S_2$. The members of this series are not yet isolated, nor does this seem likely. Further, there is a considerable amount of uncertainty as to the composition even of the end members of the series. The composition of the lowest sulphide cannot be regarded as sufficiently established to characterise the body as a chemical individual. Even the maximum of vulcanisation, in the case of ebonite, cannot be considered as established beyond all doubt.

(3) Apart from this, the phenomena observed in vulcanisation are not easily explicable on a purely chemical basis. When rubber is heated with sulphur, there is always a certain, even if sometimes very small, excess of sulphur, the "free" sulphur, left at the end of the process. It is found that the amount of combined sulphur is proportionately much greater when the total sulphur is small. Thus if the total sulphur in a mix is doubled, the amount of combined sulphur after the same cure will not be twice as great. This recalls the relationships observed for cases of adsorption.

(4) A further argument is based on the observations of Höhn that vulcanised rubber can be separated into rubber and sulphur by several treatments with a solvent such as benzene. This point does not appear to have been fully investigated in recent years.[1]

(5) Certain phenomena find a striking confirmation by the theory. For example, Axelrod showed that rubber which had been excessively treated mechanically, "overworked," showed a higher percentage of combined sulphur than a sample which had been normally treated and vulcanised under the same conditions. Ostwald considers this to be analogous to the

[1] Since the above was written, a paper by Weydert and Bary has appeared, in which it is shown that the combined sulphur is lower after treating vulcanised rubber with xylene and then isolating the rubber again.

phenomenon of "dead-rolling" observed in the manufacture of paper. It is likely that mechanical treatment by long working at a comparatively high temperature would result in a finer-grained structure, *i.e.*, in a higher degree of dispersion of the rubber colloid. This again would quite naturally cause an increased vulcanising capacity, since a higher degree of dispersion means a greater surface proportionately to the same mass, and adsorption directly depends on the surface, as it is purely a surface effect. Of course this can be explained on the chemical theory, by saying that the overworking causes a depolymerisation of the rubber, which is accompanied by a greater tendency to react with sulphur. The explanation on the adsorption theory has the advantage, as Ostwald mentions, that it lends itself more readily to experimental work, since it should be possible to measure the degree of dispersion by the ultramicroscope or other means.

(6) As far as they are available (which it must be admitted is not very far) the quantitative researches which have been made on the velocity and extent of vulcanisation are in agreement with the theory.[1]

In the case of hot vulcanisation experiments have been made by Weber, Stern, Hübener and Bysow. Weber cured thin sheets (of a mix of 100 parts rubber with 10 parts sulphur) under water in an autoclave for various periods. He opened the autoclave for the purpose of withdrawing samples every half-hour. Although he states that the time-error thus introduced does not exceed a certain amount, the method cannot be considered as quite free from exception, since it is not absolutely certain that the result will be the same as if a "straight cure" had been performed for each time-period. The rubber was cut into thin shreds and extracted with acetone till one day's extraction failed to remove any free sulphur; as will be seen later, it is hardly possible in a reasonable time to extract sulphur so completely that *no* free sulphur is removed after further extraction, although this free sulphur can be depressed to a very low figure. The combined sulphur was finally estimated by the Carius method. The curve representing the relationship

[1] See *India Rubber Journal*, 1910 (40), 247.

between time of cure and percentage of combined sulphur showed curious kinks in the case of Para. The experiments were performed at various temperatures; Ostwald calculated the increase in the velocity of combination between sulphur and rubber for each 10° C. The mean increase was on the whole more in agreement with that usually found for adsorption processes (factor = 1·5) than for chemical processes (factor = 2 – 3·5).

Hübener worked on ebonite, using analytical methods which now appear somewhat uncertain (*i.e.*, estimation of free sulphur by bromine).

Stern dissolved rubber in molten naphthalene in which sulphur was also dissolved. The mixture was heated in a thermostat at a definite temperature, and portions were withdrawn after various times. The molten mixture was allowed to run into a large volume of acetone, and the precipitated vulcanised rubber was extracted with acetone till a portion no longer blackened bright pieces of copper on heating, when it was assumed that free sulphur was completely removed. The combined sulphur was then estimated. This method is admirable theoretically, but somewhat remote from practical conditions. Nevertheless it gave interesting results, which agreed with the formula for adsorption processes (see p. 104).

Bysow took mixings of rubber with various percentages of sulphur and cured them till approximate equilibrium was attained —*i.e.*, till the combined sulphur only increased very slowly on further heating. [They were then over-vulcanised from a technical point of view.] The curve representing the relationship of combined sulphur and total sulphur agreed with that required by the adsorption formula.

Studies have also been made on the cold cure process. Bysow showed that the combined sulphur in thin sheets of Para dipped in dilute sulphur chloride solutions varied as would be expected for a process of adsorption. Hinrichsen and Kindscher worked with solutions of purified rubber and sulphur chloride in dry thiophene-free benzene. It had been previously shown by Hinrichsen and Meisenberg that, by working with purified Para in benzene solution and precipitating with an excess of sulphur chloride in benzene, it was impossible to confirm the results of

Weber, who obtained a precipitate of the constant composition $C_{10}H_{16}S_2Cl_2$ after extraction with acetone. Hinrichsen and Kindscher then showed that these precipitates contained insoluble sulphur (see p. 86), by extraction with ammonium sulphide. Accordingly they decided to work by an indirect method to determine the amount of sulphur chloride left, and thus to obtain by difference the sulphur chloride consumed by the rubber. Known amounts of rubber and sulphur chloride in benzene were allowed to react for periods of three weeks, duplicates being left for four weeks. After this time a known amount of the clear liquid was pipetted out into a flask provided with a reflux condenser. This was connected with two vessels containing alcoholic soda, and a guard tube with silver nitrate. After most was distilled off, alcoholic soda was again added and further distilled. It was found that no chlorine had escaped into the guard tube. The different lots of alcoholic soda were mixed, filtered, and the chlorine estimated by silver nitrate. In this way the residual sulphur chloride in the liquid could be determined; knowing the amount originally added, that used by the rubber was obtained by difference. It was found that the amount of sulphur chloride consumed was independent of the excess used; the composition of the precipitate was thus shown to be constant. The formula deduced was $(C_{10}H_{16})_2S_2Cl_2$, in direct opposition to the result of Weber, which they ascribed to the presence of insoluble sulphur in his precipitates; the constancy of composition of these precipitates must have been accidental.

At first sight it would seem that the results of Bysow, and of Hinrichsen and Kindscher, were discordant, since the latter deduced the existence of a compound $(C_{10}H_{16})_2S_2Cl_2$ of constant composition, while the former concluded that adsorption occurred. Ostwald pointed out that this discordance was only superficial, since Bysow worked with dilute solutions, in which adsorption effects are clearly perceptible; Hinrichsen and Kindscher worked with concentrated solutions, in which the amount of sulphur chloride adsorbed by the rubber has practically reached constancy. The coincidence of this maximum amount of adsorption with the proportions demanded by a chemical formula is not unknown in other cases of adsorption.

The quantitative measurements thus afford some support to the theory. It may be added that recently Spence and Scott have published some experiments which show that the removal of free sulphur by acetone is a much slower process than has been supposed, but that ultimately a limit is reached. They conclude, therefore, that this limit represents chemically combined sulphur, and from the velocity of extraction of the free sulphur they consider that at all events a portion of *this* is adsorbed. One is inclined to doubt whether this slowly removable portion was really all adsorbed; it may be partially due to the slowness of solution of insoluble sulphur.

The chief difficulty of the theory is to explain the fact that vulcanisation is not a reversible process, while adsorption usually is. The impossibility of removing combined sulphur by acetone points very strongly to the occurrence of some chemical change, though Ostwald has said that cases of adsorption are theoretically possible in which it would be practically impossible to wash out the adsorbed substance. At the same time he points out that the theory was put forward to explain the *taking-up* of sulphur in vulcanisation, and not necessarily what occurs afterwards.

On the whole, it seems most likely that adsorption occurs first but that the adsorbed sulphur is then chemically fixed by combination at the double bonds of the rubber molecule.[1] Freundlich has recently expressed a similar view with reference to tanning, when he says "besides adsorption, there probably occurs a further chemical action between the hide and tanning material. The greater part of the tan is adsorbed by the hide in a very short time, but this fresh mixture of tan and hide powder has as yet no leathery properties; it is only after many days that it becomes hard, 'tanned,' without much more tanning material being taken up. Other properties also change; for example, the hide powder freshly charged with tan is still easily soluble in alkalies, whereas an older one is not."[2]

This passage naturally suggests a reference to the phenomenon of "after-vulcanisation," an expression used to denote a slow

[1] *India Rubber Journal*, 1910 (40), 531, Potts.

[2] Quoted in *The Rubber World*, 2nd Feb., 1911.

increase in vulcanisation after cure has been effected. It was at one time considered that vulcanisation could only take place at or above about 247° F.[1] Hinrichsen has recently shown, however, that when various partially vulcanised (semi-cured) mixes were stored at different temperatures, an increase in combined sulphur occurred. This was especially noted at temperatures of 80°—90° C. The present author has made some experiments at 100° C. on a mixing (of Para and sulphur only) which was previously uncured. On heating a mixture (42 per cent. S) to 100° C. (not rigidly excluding moisture) for one week, it was found that the combined sulphur was about 2 per cent., after sixty hours extraction with acetone. Whereas the original mixing was soft, after heating it was what a rubber worker would term "semi-cured"; the rubber rolled out in very thin sheets, which did not adhere to one another, even after prolonged extraction. A mixing of equal parts of Para and sulphur, on heating to 100° C. for three weeks, gave a rubber which "crumbed" when rolled. By rubbing in a mortar it could be sieved. After extraction with acetone for sixty hours the combined sulphur was about 15 per cent. These appear to be the first published data on the vulcanisation of an uncured mixing of rubber and sulphur alone at temperatures as low as 100° C. They do not absolutely prove that insoluble sulphur was not present, but from the nature of the results and the physical appearance of the specimens, it seems clear that vulcanisation had occurred. At all events, the point as to insoluble sulphur is one which has been scrupulously neglected in practically all researches. It now seems generally accepted both technically and scientifically that vulcanisation can occur at much lower temperatures than 247° F., though even yet there is scarcely agreement as to precisely how high a temperature is sufficient to cause a measurable effect, even within a time of six months.

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The vulcanisation of rubber articles in practice is a very different matter to the simple reactions of the laboratory, since such a large number of variable factors come into play. Quite apart from such variables as the kind of rubber employed in the

[1] In the absence of accelerators, such as litharge.

mixing, the nature and amount of the mineral and organic fillers, the percentage of sulphur, and the actual condition of the compounded rubber due to mechanical treatment and other cases—vulcanisation is still a more complex phenomenon even than would be expected from such a remarkable reaction. Assuming for the moment that the above factors are all constant, in other words taking a particular batch of a given standard mix, a correct cure will depend mainly on the following factors:—

(1) The method of applying heat, by hot air, direct steam, etc.

(2) The temperature and time of the cure.

(3) The shape and size of the article.

(1) Rubbers for various purposes require very different methods. Hot air (used very largely for galoshes), does not give the same result as steam, being slower and more variable, on account of its lesser conductivity for heat. This factor comes into play in the case of steam to a certain extent. The cure will depend on the wetness or dryness of the steam, and patents have been taken out for means whereby the steam should be made quite uniform in this respect. In practice, it very often happens that where such devices are not employed, curious discrepancies are observed in successive cures, where conditions appeared identical, and these discrepancies are to be attributed to the variations in the steam.

As Schidrowitz has pointed out, steam probably exerts some specific action. The present author has come to the same conclusion, as a result of numerous vulcanisation experiments in which the free or combined sulphur was estimated. In such experiments it is also found that the total sulphur is usually low when steam has direct access to the sample. It is thus by no means immaterial whether the articles cured in live steam are wrapped in cloth or in tinfoil. In the latter case, owing to exclusion of direct access of the steam, the combined sulphur is usually found to be lower, though of course the tightness of the wrapping may influence the result. Both this point and that as to dryness of steam are extremely important in considering the results obtained in experimental work on a small scale (see p. 127).

(2) Time and temperature.

When no accelerators are present the velocity of curing at a given temperature is proportional to the amount of sulphur present. The amount of combined sulphur increases with the time of cure (see p. 108) but not directly. After a certain percentage of combined sulphur has been reached the increase may be very slow indeed. The velocity of cure increases in the ratio of 1 to $1\frac{1}{2}$, or 1 to 2, per 10° C. (18° F.). [Calculated by Wo. Ostwald from Weber's data.] [1]

Soft rubbers are frequently cured at one temperature, with a "rise" of so many minutes. In the case of ebonite, however, a series of temperatures are usually employed, so that it is difficult, if not impossible, to make more than approximate calculations of what is taking place, except as the result of experience.

As will be seen later, the properties of a rubber cured to the same percentage of combined sulphur at two different temperatures are not necessarily the same.

(3) Shape and size of the article.

Two factors are involved here, the thermal conductivity of the mix (both in the uncured and cured condition, since vulcanisation will not proceed at the same rate throughout the mass), and the heat of reaction between the sulphur and various constituents of the mix, especially the natural resins of the rubber.

Rubber is not a good conductor of heat, and there is consequently a lag in temperature from the outside inwards. To a certain extent this is overcome by the "rise," but by no means entirely. Thus if a thin rubber, say 25 mils ($\frac{1}{40}$-inch), is cured for two hours with half an hour rise, it is probable that the temperature during cure will be fairly uniform throughout. If, however, a thicker rubber (1 inch or more) is being cured, even though the rise is prolonged the outside may begin to cure long before the inside. In the case of an ebonite of any considerable thickness it may take from one to two hours before the inside reaches the temperature of the outside.

The heat of reaction between sulphur and constituents of the mix is a most important factor, especially in the case of thick articles. That such a disengagement of heat occurs may be

[1] Though below the melting point of sulphur the velocity is probably very much less proportionately.

recognised not only from special experiments, but already from the simple fact that large sizes of ebonite may be cured at much more gentle cures than small sizes, *e.g.*, if a $\frac{1}{16}$-inch sheet and a 1-inch sheet are simultaneously cured, the thicker sheet may be overcured while the thinner one is undercured, despite the longer time which would normally be required to heat up a thick sheet. This phenomenon is intimately connected with the theory of the action of accelerators of vulcanisation. It has been shown that the heat of reaction between sulphur and rubber itself is small. Thus Bysow found that the heat of combustion of a certain mix was practically the same before and after cure, showing that no energy change had occurred in that operation. Therefore, the heat evolved cannot be due to the reaction of vulcanisation itself.

The part played by litharge (and inferentially by other accelerators) in hastening vulcanisation was obscure for a long time, till Esch and also Seidl showed that the action consisted in the stimulation of a reaction between sulphur and rubber resin, which evolved much heat. Seidl examined mixtures of resin, sulphur, and litharge, and showed that at vulcanising temperatures these mixtures gave out considerable heat. He also took mixings of purified Para and ordinary Para with sulphur and litharge, and found that the latter vulcanised faster, and that when a thermometer was placed in the mixing heated to vulcanising temperatures, the mixing with ordinary Para showed a rise in temperature, while the purified Para mixing only showed a very slight rise. A mixing with ordinary Para, zinc oxide, and sulphur behaved similarly to that of purified Para, litharge, and sulphur, so that it was evident that the action of litharge was to bring about a reaction with the resin and sulphur which evolved heat; this raised the temperature of the mass above that of the surroundings, and thus caused vulcanisation to occur more rapidly. The explanation appears satisfactory and complete.

Thus when a mixing containing an accelerator is cured at a given temperature, vulcanisation is really proceeding at a higher temperature. This higher temperature is attained especially in the centre of the article.

As a result of the combined action of the low thermal con-

ductivity of rubber, and this heat of reaction due to resins and sulphur under certain conditions, it is well-nigh impossible to say what are the temperature conditions in a large sample throughout the period of cure, especially when the temperature is gradually raised.

In what has been said hitherto it has been assumed that the article is homogeneous. The difficulties are increased when we come to deal with "built-up" articles, such as tyres or cables. In these cases it is desired to cure different layers properly, but it is also desirable to arrange matters so that no great excess of sulphur is present. It is, of course, easy to grade the mixings, so that the inside layer will cure equally with the outer one, by increasing the proportion of sulphur in that layer.[1] This is not advisable, since in that case the inner layer will contain a large amount of free sulphur. This may wander, on keeping, and may deposit at the interface between the two layers. Even if this does not occur the deposition of this free sulphur is very liable to take place in patches. The presence of such nodules disseminated throughout the mass is likely to promote decay, since these points of unevenness must tend to be sources of weakness. Again, as was pointed out in the *Jahrbuch der Kautschuk Industrie* (1910), the presence of much free sulphur in articles which are liable to be subjected to friction (and consequent heating) will probably lead to a dangerous after-vulcanisation, which may ruin the rubber. An alternative method of grading the mixings for the layers of built-up articles lies in the use of accelerators. The ideal design would be one in which the proportions of accelerator and of sulphur were so carefully adjusted throughout, that each layer would be perfectly cured, and yet would contain very little free sulphur.

Some common faults due to imperfect vulcanisation may be considered. "Blooming" is a separation of sulphur at the surface of an article. It is due to the wandering of an excess of sulphur in the free state. Remedies are boiling in caustic, or diminishing the amount of total sulphur and readjusting the cure.

[1] In cables the "separator" or layer next to the "pure", has less sulphur than the outer layer, the "jacket." This is designed, however.

"Porosity" may occur as small holes in the interior of the article. This is a very common defect, due often to too rapid rise of temperature, or to presence of moisture in the mixing. Hence arises the importance of careful moisture estimations on all ingredients. Various ingredients are added to mixings as remedies.

Under-vulcanisation and over-vulcanisation[1] are both to be avoided, but the latter is more dangerous—also, once an article is over-cured it cannot be made right, whereas an under-cured article can be re-cured.

While it is very important to be able to define numerically the correct degree of vulcanisation, the determination of combined sulphur is not in itself sufficient. As Weber himself pointed out, the same coefficient of vulcanisation may represent different extents of cure, according as the rubber has been cured at different temperatures. Axelrod explained this by assuming that during vulcanisation two processes occurred in the rubber:—

(1) Depolymerisation by heat.

(2) Polymerisation by sulphur.

Since these two processes may take place at different rates, it is possible to explain the kinks in Weber's vulcanisation curves, since on this ground it would not be expected that vulcanisation would occur regularly throughout, as it would depend on which of the above processes predominated at the time in question. The properties of the product naturally depend on any changes in extent of polymerisation (or degree of dispersion). Nevertheless, the determination of the coefficient of vulcanisation is very useful, especially when comparing similar cures.

Experimental work on vulcanisation is rendered difficult by the many complications which occur on the large scale. On a small scale these are difficult to reproduce. If a small autoclave is used the steam is likely to be more damp, and thus the rate of cure will be affected. If a small mix is made, it will tend to be "overworked" in the mixing operation; it will thus be too soft, and will not give the same results as a large-scale mix. There are two main lines of work. Chemical analysis may be used as a

[1] See "Chemistry of India Rubber," Weber, for detail.

means of control for works practice, and vulcanisation tests may be made on samples of raw rubber.

In the first case it is best to select methods of testing the product mechanically or otherwise; when a suitable result has been obtained the coefficient of vulcanisation is estimated; this will then serve to some extent as a standard for that particular purpose. Or the properties of samples of different known coefficients of vulcanisation may be measured, when the desired properties may be calculated from a curve expressing this connection.

In the second case samples are made up to a standard mixing formula.

A common practice is to add 10 per cent. sulphur, which is rather remote from works practice as a rule; a better mixing would be one containing only about 50 per cent. rubber, with mineral fillers. Such a mixing, if well cured, can be "crumbed" for analysis, which is a further advantage over mixings of much higher rubber content.

Pieces of a standard size are cured under absolutely standard conditions—either in a press or in live steam, in which case the wrapping should always be the same. The vulcanised rubber is then tested mechanically, and also for combined sulphur (see Chapter VI). It must be remembered that such small mixings are liable to be "over-rolled," *i.e.*, over-worked. The compounded rubber will thus be softer than a large-scale mixing made on the same formula.

LITERATURE.

Weber's "Chemistry of India Rubber" contains much practical information on the chemical aspects of vulcanisation. Manufacturing details will be found in works such as that of Esch and Heil, and others. As far as the theory of vulcanisation is concerned, the discussion has been full, as the researches bearing on the subject are of such recent date.

CHAPTER VI

VULCANISED RUBBER

VULCANISED rubber represents the technically important derivative of raw rubber. In practice the term is used to denote any rubber mixing which has been vulcanised; thus, in vulcanised rubber we are not only concerned with the modification of properties caused by the operation of vulcanisation itself (see Chapter V), but also with the various effects produced by the compounding ingredients which have been used (see Chapter IV).

As far as the modifications induced by vulcanisation itself are concerned, it will be clear from the previous chapter that they really resolve themselves into a question of greater stability—a stability to chemical change, and also to various physical influences, more especially to heat and mechanical stresses of different kinds. That is the working effect, so to speak. The theoretical aspect of the whole case has undergone curious vicissitudes. Leaving out of consideration the period of wild hypothesis, it is remarkable that at the present time the most important and far-reaching of Weber's views (as expressed in his famous "Outlines of a Theory of Vulcanisation") are really those which consider rubber from the colloidal standpoint. His series of rubber sulphides cannot be accepted now; but his conception of vulcanisation, as a process whereby the physical condition of raw rubber was perpetuated, still remains exceedingly luminous and fruitful. In fact, if we translate this view into the language of the colloidal chemistry of the day, we will find it very helpful to consider vulcanisation in this way. Looking at it thus, it seems best and safest to regard vulcanisation as a process of coagulation, though not in the same sense as with latex. What is meant is that raw rubber is a body more of the sol type (see p. 11); it is comparatively readily soluble and behaves as a typical

emulsoid colloid.[1] It is "coagulated" by vulcanisation, with the usual results attending the formation of a gel. This implies greater stability; particularly does it imply lesser solubility, which is one of the great characteristics of vulcanised rubber, for we find that, while raw rubber is not always easy to bring into colloidal solution, vulcanised rubber is often almost intractable in this respect. Further, the difficulty of solution increases as the coefficient of vulcanisation increases, till at length in ebonite we reach a body very resistant to practically all organic solvents.

In this and other ways the behaviour of vulcanised rubber agrees very well with the assumption that the rubber colloid has been coagulated during vulcanisation. The gradual formation, in increasing amount, of rubber sulphides does explain these changes to a certain extent, because we know from other examples that an unsaturated body is more capable of reaction, *i.e.*, more energetic chemically, than a saturated one. If vulcanisation depends on the gradual addition of sulphur at the double bonds of the rubber hydrocarbon, it naturally must bring about a saturation of the compound, resulting finally in an ebonite $C_{10}H_{16}S_2$ in which there are now no double bonds available at all.

As far as the alteration in properties due to the compounding ingredients is concerned, this is a matter of great complexity, on which something has been said in Chapter IV.

* * * * *

Chemical work on vulcanised rubber necessarily covers a very wide area, comprising control, obtaining data for the production of goods similar to a sample, valuing samples, explaining faults in articles which have been in actual use and, more generally, experimental work in the direction of securing desired qualities in the product.

For all these purposes it is necessary to be in possession of methods of analytical attack, for the estimation of various constituents. Also chemical methods of testing for durability are used, and finally mechanical tests of the strength, elasticity,

[1] As compared with the rubber globules in the latex, raw rubber is more of the gel type; as compared with vulcanised rubber, however, it is certainly of the sol type.

resistance, etc. Microscopical studies of vulcanised rubber have been made by Breuil and Ditmar, and the method deserves more general attention. As far as the mechanical tests go, they are of vast importance, yet they cannot be classed as chemical, and will not be discussed here. References will be found at the end of this chapter to works dealing with the subject. It has been said that the function of mechanical tests is to detect errors in the manufactured article: it is the function of the chemical tests to explain these errors. There is much truth in this, and it will be found that chemical tests alone are insufficient for many purposes. But within the wide range indicated above there is no doubt that chemical methods are of great value. It is best, however, to face one fact clearly. Even when a full chemical analysis has been made of a sample of unknown composition, the results are not sufficient to enable the article to be duplicated immediately; in many cases they would not be sufficient to effect this object at all, except after very laborious experiments in compounding and vulcanisation. Thus even an accurate determination of the rubber content of an article of vulcanised rubber will leave us in great doubt as to the condition in which that rubber has been added to the mixing. We may be quite unable to give the percentage of reclaimed rubber (containing a certain percentage of "rubber substance") which has been added in the case of a soft rubber, or the percentage of ebonite dust (powdered ebonite) which has been added in the case of an ebonite. Further, we shall often be unable to give more than a very approximate indication of the brand of raw rubber which has been added. Unfortunately, it is precisely points such as these which are often of vital interest to the manufacturer. Nevertheless, more can be done now than even a few years ago, and after all, the main object of the chemist is not so much to find out exactly how a certain article *has* been made, as rather to discover how an article of equal or better quality *can* be made. A rational knowledge of the theory of vulcanisation itself, and of the functions of the various fillers, must help here, and when this is coupled with increasing perfection in the difficult art of analysis, the future possibilities are considerable.

* * * * *

ANALYSIS.

A consideration of the methods of raw rubber analysis is sufficient to show that this is one of the most difficult branches of analytical work. When we come to vulcanised rubber, we find almost all these difficulties in an aggravated form, so that the analysis of vulcanised rubber is an exceedingly complex operation, requiring the utmost skill, care and experience. Thus in working on raw rubber difficulty is often experienced in dissolving the sample; in vulcanised rubber such solution may be practically impossible.

The methods of rubber analysis were first developed to a more or less satisfactory condition by R. Henriques. His work was continued and elaborated in a very full way by Weber, to whom this branch of the subject also owes a great debt. The methods of analysis at present in use are still largely based on the work of Henriques and Weber; though subsequent research has both introduced new methods and invalidated old ones, yet much of our procedure can be traced directly to their work.

The constituents of rubber goods may be analytically classified as follows :—

Mineral Matter.	Organic Matter.					Sulphur and Chlorine.
"Ash" is the approximate estimation by simple incineration of the sample. Certain mineral constituents are separately determined.	Resin Group.	Bitumen Group.	Substitutes	Other Organic Matter.	Rubber	Both may occur in various groups; sulphur may also be present "free."

Sampling and Preparation for Analysis.

Before analysis, the sampling and preparation of the rubber are of great importance. In connection with sampling, it must be assumed always that the sample may not be homogeneous—

great inequalities may result from faulty mixing, wandering of sulphur, loss of sulphur on the outside, inequalities of cure, presence of French chalk on the outer layers and other causes. Thus the operation must be done very thoroughly and conscientiously. If possible it is best to break up the whole sample between a large pair of works rollers, and then to sample the finely divided product.

The sample should be prepared for analysis by being as finely divided as possible. Ebonite can be filed with a fine file; the powder should be as fine as possible. Soft rubber should be worked between a small pair of rollers till it is broken up, and then rubbed well in a mortar. This procedure answers admirably for a mixing (not undercured) containing less than 50 per cent. of rubber. If much more than 50 per cent. of rubber is present, and the rubber is not heavily cured, it will only sheet. In this case, it should be rolled out again and again till the thinnest possible sheets are obtained.

The fineness of division requires to be the greatest for acetone extraction and rubber estimations. For most total sulphur estimations, rather coarser material is not disadvantageous.

Determination of Acetone Extract.

We will consider first the separation of the organic matter into groups; the first operation here is that of acetone extraction, by which free sulphur, with the resins and oils, waxes, etc., are removed. Portions of subsequent groups are also removed by this extraction.

The general principles of acetone extraction have been discussed in Chapter II. The time of extraction is an important consideration. It may be noted first that it is practically impossible by extraction in a soxhlet to arrive at a point when no further extract is given. By the extraction of four samples of ebonite for successive periods of ten hours the author found that a slight extract was being given even after eighty hours extraction. In the same way, Britland and the present author have found that soft vulcanised rubber still yields an extract after very prolonged extraction. In all these cases, needless to say, not corks, but ground glass connections were used. This cannot be

attributed in normal cases to any polymerisation of the acetone itself, although such an action does occur when the acetone is treated with lime or calcined magnesia. This action may occur in the extraction of certain rubbers, but even then the product of polymerisation is a liquid, which does not leave behind, on prolonged drying, a very large solid residue. Evidently, then, it is almost impossible to extract vulcanised rubber till absolutely no more extract is given. Again, as far as free sulphur is concerned, it was found that the amount removed between the tenth and twentieth hours was very small for a number of rubbers. Spence has shown that the complete removal of sulphur may require a very long time. Whether this is due partly to the small solubility of sulphur present in the insoluble form (see Chapter IV) is a question which has not been very fully considered.

The upshot of considerations of this kind is that it is necessary to extract in a definite way for definite periods of time. The period recommended for soft rubbers by the Königlich Materialprüfungsamt is ten hours, and for commercial purposes the general use of this period is advocated here. The amount removed in a second ten hours is certainly appreciable (with a soxhlet of 100 cub. centimetres capacity, ranging from 0·2 to 0·3 per cent. on 5 grammes, from the results of Britland and the author), but nevertheless, as explained above, it is practically impossible to extract completely; the results will be comparable; and finally, 0·3 per cent. is not a very great error for technical rubber analysis. The extractor recommended is the Zuntz, and in connection with it extraction flasks with mercury seal; the condenser is attached to the extractor by a ground glass joint. A battery of such apparatus is useful, and there is the advantage that practically any flask will at once fit any extractor, which means a very great saving of time. To distil these flasks down a small bent tube is used, of which one arm fits into a condenser by a cork, while the other wider arm fits on to the mercury sealed flask.

For ebonite, Weber recommended two days' extraction on account of the difficulty of removing the sulphur. Although extraction will not be complete, this period can scarcely be

extended, and even if it were, the result would not be quite correct. Consequently, it would be well if a standard period were fixed for this purpose. A twenty-hour extraction is satisfactory. The author is at present making trial of a new method of extraction, which appears to yield promising results. It consists in heating the ebonite with acetone in a sealed tube or bottle at 100° C. for one hour, and then extracting for a short time. The method is much more rapid than ordinary extraction, but it appears to remove rather more. From what has been said above this may not mean that it is extracting rubber also, but that it is removing difficultly soluble resin. In any case it seems worthy of trial. Theoretically, it appears likely to dissolve "insoluble sulphur" more rapidly.

When extraction has been continued for the specified time, the acetone is distilled off, and the flask is dried till constant at 105° C., best in a gas oven. If much free sulphur is there, care must be exercised in heating. It is well to emphasise the fact (noted already in Chapter II) that a flask must not be rubbed before weighing, otherwise the weight will be too small, unless time is allowed to dissipate the electric charge.

The total acetone extract mainly contains resins, free sulphur, wax, oil, etc., together with the soluble portions of organic fillers such as rubber substitute or M.R. A complete separation is impossible. What can be done is to estimate the wax and free sulphur, and to determine the optical activity, which may enable some conclusions to be drawn as to the kind of raw rubber which was originally used in the mixing (see p. 55).

Estimation of Free Sulphur.

Free sulphur is estimated by oxidation with fuming nitric acid, and transformation of the sulphuric acid thus formed into barium sulphate. As the treatment with nitric acid alone is hardly sufficient, the organic matter present is usually destroyed by ignition with fusion mixture. The full details of the process are as follows:—

A small watch-glass, or a funnel cut short at the neck, is placed on the flask. Fifteen to twenty-five cub. centimetres fuming nitric acid are added from a burette, wetting the flask all over inside. If

the action is violent the flask is cooled under the tap. The flask is then heated very gently by placing it on a clock-glass heated by a boiling water-bath. It is of the utmost importance to moderate the action at this stage. When practically all the yellow particles of sulphur have disappeared, the flask is heated direct by the steam until no particles are left. On no account should the sulphur be allowed to oxidise very rapidly, throwing up rapid bubbles of gas. If this occurs loss of sulphur is taking place, probably as SO_2. Thus it is necessary to regulate the heat applied so that the sulphur disappears slowly and gently, with as little bubbling as possible. Otherwise, as the present author has shown by numerous experiments on the oxidation of sulphur, serious losses may occur.[1] Once all the free sulphur has disappeared, there is practically no danger of losing sulphuric acid by volatility at water-bath temperatures, as he was able to show by working on pure sulphuric acid. Even on evaporation to a thick syrup and heating on the water-bath for a considerable time there is no appreciable loss. Statements in the literature about volatility of sulphuric acid are to be explained almost entirely by losses which have occurred during the oxidation of the sulphur, as shown above.

After all the sulphur has disappeared, the liquid in the flask is poured into an evaporating basin (3 inches) and the flask is rinsed three times with fuming nitric acid, if necessary heating once or twice. The author finds it very convenient to use a burette filled with the acid for this purpose: there is no danger of spilling the acid, and it is possible to rinse the whole inner surface of the flask with about 2—3 cub. centimetres. To aid in pouring from the flask, especially if a mercury seal flask has been used, a short rod is used. This is retained in the basin for subsequent use. If a mercury seal flask is used in which the inner tube does not project far enough from the outer one to enable pouring to be effected, it is necessary to use a rod bent at a right angle. This can then be washed and replaced by a short straight rod. Such flasks are better avoided, in favour of those where the inner tube projects a fair distance.

[1] Potts, in "The Rubber Industry," the Report of the International Rubber Conference, 1911.

The liquid in the basin is evaporated on the water-bath to a thick syrup. It is then intimately mixed with 2 grammes fusion mixture (5 parts sodium carbonate, anhydrous, to 3 parts potassium nitrate).[1] A few drops of warm water may be used if required. The powder should be rubbed round the sides of the basin, and the greatest care exercised in thoroughly mixing. After removing nearly all the mixture from the small rod, this is taken out and kept aside. A basin is placed over the basin containing the mixture. This is placed in a hole cut in an asbestos board (to exclude access of gases from the flame, which contain sulphur) and slowly heated by a small flame, which is gradually raised from time to time; care must be exercised to avoid "firing." When the mass in the basin is practically all white, it is strongly ignited. This is best done by heating for a few minutes in the muffle. The rod is rubbed in the heated mixture to oxidise any mixture upon it. Any particles which spurted into the basin used as a cover are also added. Great economy in basins can be effected by stirring the pasty mass in the basin as it solidifies, by which means the liability to crack is much diminished.

After cooling, the contents of the basin are transferred to a 600 cub. centimetre beaker; the rod is washed, and 10 cub. centimetres conc. nitric acid are added. The liquid is evaporated to dryness on the hot plate (avoid flame gases); 5 cub. centimetres dilute *HCl* (1 to 4) are then added, and after dilution with water the liquid is filtered. The filtrate is made up to about 200 cub. centimetres, 8 grammes of potassium chloride are added, and the liquid is boiled. Precipitation is effected by the addition of about 2 cub. centimetres excess of 10 per cent. barium chloride solution, added rapidly drop by drop from a burette. After standing (over night if possible, though no great error is introduced by filtering after a half to one hour) the precipitate is filtered, washed twice by decantation, and then on the filter with hot water till the washings show no turbidity with silver nitrate. The filter is dried from superficial moisture by a clean towel or by filter paper, folded and placed wet in a weighed porcelain

[1] If the acetone extract is more than about 0·4 grammes, use more fusion mixture if required, and increase the *KCl* added later proportionately.

crucible. This is heated *at the threshold* of the muffle till the filter paper is well carbonised. It is then ignited, cooled in air and weighed (cooling in a desiccator is unnecessary for 1-inch crucibles).

$$\text{Sulphur} = BaSO_4 \times 0{\cdot}1373.$$

If desired, the precipitate may be dried, transferred, and the filter burnt dry. Under the conditions mentioned above, the author has found by a very large number of special experiments (with precipitates obtained from solutions of sulphuric acid) that no loss occurs, provided that the paper is carbonised before putting the crucible *in* the muffle. It is sometimes stated that barium sulphate precipitates should not be ignited strongly. Working with small precipitates no marked loss in weight occurs, even after prolonged ignition in the muffle.

This process may be shortened when the very highest accuracy is not desired by igniting (with the fusion mixture) in the muffle.[1] If the heating is done very cautiously at the door, and the basin is then gradually pushed further in, no serious loss results. Further, the nitric acid may be added to the basin before transference to the beaker, covering with a clock-glass throughout. In this way the volume can be kept much lower.

A still further acceleration may be made by omitting the ignition, but this procedure is not recommended. It has been shown that the results are apt to be low, and the method is not so clean. In this case the liquid from the flask is transferred to a beaker instead of a basin, evaporated to dryness with 2 grammes KNO_3, and then treated as above—addition of 8 grammes KCl etc. Others evaporate to dryness with $NaCl$, and then evaporate with HCl. For the reason of the above treatment, see below.

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At this point it will be advisable to go more fully into the whole question of the precipitation of sulphuric acid as barium sulphate. The operation is not by any means the simple one which it was considered to be at one time.

A very large number of researches have appeared on this subject, including those of Richards and Parker, Gill and Grindley, Hintz and Weber, Lunge and Stierlin, Allen and Johnston, and

[1] Private communication from Dr. F. J. Brislee.

others. The special application of the principles of this precipitation to rubber analysis was considered in the paper quoted. The subject is so vast that only a general summary can be given.

When solutions of pure sulphuric acid in water, containing hydrochloric acid, are precipitated by barium chloride, it is found that correct results are obtained when the barium chloride is added slowly drop by drop. This result is due to the neutralisation of two errors :—

(1) $BaSO_4$ is slightly soluble;

(2) $BaSO_4$ carries down, or occludes, a certain amount of $BaCl_2$, which cannot be washed out.

It is clear that (1) and (2) act in opposite directions. In ordinary circumstances they balance one another very effectively.

If, however, precipitation is effected by addition of barium chloride all at once (usually 10 per cent. solution, diluted with four volumes of water, and added boiling) a high result is obtained. The error (2) is greatly increased, because the precipitate is actually formed in presence of an excess of barium chloride, contrary to what occurs when the barium chloride is added drop by drop. Thus (2) is a greater error than (1).

With solutions of sulphuric acid, then, a correct result is obtained by adding the barium chloride drop by drop.

The precipitation is a far more complex matter when comparatively large amounts of salts are present. In this case the following errors are possible.

Lowering the Result.	Raising the Result.
(1) Solubility of Barium Sulphate. (2) "Free" Sulphuric Acid in ppt. (3) Alkali Sulphates in ppt.	(4) Barium Chloride in ppt. (5) Presence of Nitrates.

(1) The solubility of barium sulphate is not nearly so large as might be imagined. This error is small. It becomes high in presence of large excesses of HCl.

(2) A small error is introduced by the presence in the precipitate of a small quantity of sulphuric acid, which is lost on ignition.

(3) A large error may be caused by the presence of sodium or potassium sulphate in the precipitate. As their molecular weight is less than that of barium sulphate, the result is decreased.

(4) Barium chloride may be contained in the precipitate, which obviously raises the result.

(5) In actual rubber analysis, a fifth error comes into play, caused by the presence of nitrates, which raise the result; the precipitate then contains barium nitrate.

The method of precipitation adopted is of considerable importance. For very accurate work it is best to precipitate with barium chloride drop by drop, and to apply suitable corrections for the various errors. For most work the rapid precipitation method of Hintz and Weber is used. About 2 cub. centimetres excess of 10 per cent. barium chloride is diluted with 4 volumes of water, and added boiling, all at once. In this case error (4) is larger, and balances errors (1) to (3). When precipitating drop by drop error (3) is largest, and thus the uncorrected result is low. These conditions hardly apply in rubber analysis where nitrates are usually present.

The ordinary procedure, almost universally adopted, is to evaporate the ignited mixture to dryness with hydrochloric acid. In this way nitrates are not usually removed completely. In the method mentioned above, that of evaporation with nitric acid, a definite amount of nitrate is formed. It has been shown by Folin, and by Gill and Grindley, and also confirmed by the present author, that the error caused by nitrates can be almost perfectly compensated by the addition of a fourfold amount of chlorides, providing that precipitation is effected drop by drop. The use of nitric acid also has the advantage that it will tend to oxidise any sulphides formed during the ignition. Curiously enough, on acidification with HCl after a "fusion," slight evolution of H_2S can occasionally be noticed. This will not be so likely to occur when nitric acid is used.

In short, we may say of the precipitation that the results are bound to be affected by errors, but that, as Ruppin has observed, we can make these errors, which are fairly constant, compensate one another. The conditions mentioned above effect a very fair compensation, and are thus recommended. But it must be noted

that if they are not all observed, errors will result. Thus if precipitation is effected by addition of barium chloride all at once, under the above conditions, too high a result will be obtained, and so on.

Volumetric Estimation of Sulphur.

Sulphuric acid can be directly titrated with barium chloride (see "Volumetric Analysis," Sutton). The author finds that at least twice as much chlorides as nitrates should be present, and that the acidity should not exceed 2 cub. centimetres dilute HCl per 100 cub. centimetres solution. Otherwise the end point is bad. This is determined by removing a portion of liquid with a Beale's filter, and testing with both H_2SO_4 and $BaCl_2$ on a mirror. Contrary to the method recommended by Sutton, the present author prefers to take as the end point the moment when the opalescence produced in each solution is equal—the liquid usually gives a precipitate with *both* reagents at or near the end point. A trial should be done with an aliquot part of the liquid, and then in a second portion about 90 per cent. of the required amount should be added rapidly from the burette. The remainder is added gradually. Using $\frac{N}{16}$ $BaCl_2$ (1 cub. centimetre = 0·001 grammes S = 0.1 per cent. on 1 gramme rubber) the end point is good to about 0·3 cub. centimetre. The presence of salts introduces an error up to 0·5 cub. centimetre. For very rapid work the method is decidedly useful, though it requires care and practice.

Other more complicated volumetric processes have been proposed, but it is hardly necessary to describe them here.

* * * * *

The "free sulphur" thus obtained is deducted from the total acetone extract.

The appearance of the extract is a useful guide. A very clean-looking resin points to the absence of rubber substitute, etc. Practice will enable valuable conclusions to be drawn in this way. The presence of mineral oils is shown by their insolubility in cold alcohol; they impart a decided fluorescence to solutions.

Estimation of Wax.

Ceresin wax may be recognised from its appearance. Several methods have been used for its estimation, based on its insolubility in cold glacial acetic acid (Weber) and on other properties.

The method of Hinrichsen and Marcusson is perhaps the best. The extract is warmed with 96 per cent. alcohol (50 cub. centimetres) and filtered, washing with 25 cub. centimetres alcohol. The filtrate is cooled one hour at − 4° to − 5° C. It is filtered (best through a cooled funnel) and washed with 100 cub. centimetres 90 per cent. alcohol, (cooled to − 4°). The filtrate is again cooled to make certain that all the wax has separated out. The wax on the filter is transferred to the weighed flask in which the cooling was done, by dissolving in warm carbon bisulphide (freshly redistilled). The flask is distilled down and dried till constant at 105°. The sulphur which has partially passed into this wax is determined as above; this will be lower than the "free sulphur", which must be determined in a separate extract. After deducting the sulphur, the weight of wax is obtained.

A blank should be done with the same amount of wax, and a correction applied for the solubility of the wax. Working with absolute alcohol, and taking 0·15 grammes wax, W. J. Britland and the author find that only 0·135 grammes are obtained. About 3 milligrammes of this separate out on the second cooling.

When no rubber substitutes, etc., are present, the acetone extract, less free sulphur, less wax, is called "resin". The resin is usually greater than that calculated from the nature and amount of the raw rubber used in the mix, *i.e.*, on vulcanisation an apparent increase in resin content occurs, as Weber first pointed out.

Dichlorhydrin Extraction.

Certain hard resins, occurring sometimes in ebonite, are dissolved by dichlorhydrin. For this purpose the acetone-extracted rubber is heated with the solvent. The author heats with a definite volume of dichlorhydrin at a definite temperature, and filters and washes the ebonite on a weighed Gooch crucible. The estimation must be done by difference, since it is

not easily possible to recover the resin from the solution, on account of the high boiling point of the solvent (171°).

Dichlorhydrin dissolves portions of the bitumen group also, as well as a small quantity of rubber. The estimation is thus but an approximation.

Detection and Estimation of the Bitumen Group.

The old method, which may be still found in many books, is that of pyridine extraction, following the acetone extraction. It has been shown by Esch, Ditmar, and Britland and the author, that this method is unreliable, since rubber is readily dissolved. For this reason it is to be discarded. Comparative analyses of samples with and without bitumen proved that the method was useless. For the estimation of M.R., Becker recommends extraction in a Zuntz apparatus for one hour with carbon bisulphide, which does not appreciably dissolve rubber in this time, although it swells it—a result which the author can confirm.

Cold pyridine may be used as a qualitative test for these bodies, which impart a very dark colour to it. Henriques used cold nitrobenzene as a quantitative method, and Britland and the author consider that this method is worthy of more trial, although it has been neglected since the hot pyridine extraction "superseded" it.

Estimation of Rubber Substitutes.

The acetone extracted rubber tends to oxidise very rapidly, and must not be dried in an air oven, nor must it be allowed to stand in contact with air. Thus a sample of acetone-extracted rubber kept in a desiccator for three to six months became quite hard and brittle, and yielded an enormous acetone extract, which was dark, oily, and evil-smelling.

The estimation of rubber substitutes must thus be performed immediately, unless the extracted rubber is preserved in vacuo. It may be dried in vacuo, or in coal-gas. It is then boiled for four hours with 100 cub. centimetres $\frac{N}{2}$ alcoholic soda and

washed with hot alcohol and hot water. In this way (see p. 79) the substitutes are removed.

The estimation can be performed in two ways. First, the rubber can be treated as above, and the fatty acids can be separated from the filtrate. This method is recommended by Hinrichsen and Marcusson. The liquid is evaporated down to about 15 cub. centimetres, diluted with water, acidified with dilute sulphuric acid, boiled, cooled and made up to 100 cub. centimetres. It is extracted with ether several times, and the ethereal extract is washed with water. On evaporation in a weighed flask the amount of fatty acid is obtained, which practically represents the weight of substitute. It is stated that a good rubber will yield about 0·5 per cent. extract in this way. The author finds that this figure is obtained, and that the method works satisfactorily.[1] A blank may be done if great accuracy is desired, since the alcoholic soda always yields a residue in this way. If it is desired to avoid corks, a mercury seal flask may be used, on which is placed the wide end of a condenser. The heating is performed in the water bath under this reflux condenser.

The alternative method is that of weighing the rubber before and after treatment, and reporting the difference as substitute. Weighing should be done till constant. It should be added that it is excessively difficult to wash the rubber free from alkali, even when it is repeatedly boiled with water. It is not enough to test the wash water: if the rubber is white it should be tested itself with phenol-phthalein. In any case, it is safer to ash the rubber after treatment and to compare this result with that obtained on a portion of the rubber before treatment. If, after allowing for the substitute removed (if any), these ashes are not equal, a correction must be made. Not only may caustic soda be present, but certain mineral fillers may have dissolved out. In normal cases, however, the rubber may even weigh more after treatment than it did before, since the caustic soda adsorbed may be greater in amount than the

[1] Two extractions on a rubber containing 3 per cent. rubber substitute gave results between 2 and 2½ per cent. As the substitutes which had been used in the mix gave acetone extracts from 16 to 30 per cent., the agreement is satisfactory.

matter dissolved by the alcoholic soda. It is safest in important cases to work by both methods—the difference method and that of acidification and ether extraction. A second treatment with fresh alcoholic soda is advisable if much substitute is present.[1]

Estimation of Mineral Matter.

The determination of the amount of the mineral constituents is an operation of the greatest importance. When rubber is estimated by the difference method this estimation must be performed with the utmost accuracy. For this purpose it is necessary to dissolve out the rubber. In many cases, a fair approximation can be obtained by "ashing" the sample, although this is a somewhat crude method. The results of duplicate determinations are often extraordinarily close, but these results may still be quite erroneous, owing to the presence of volatile mineral constituents, or to constituents which alter in weight on heating. Despite this lack of universal accuracy, the method is often very useful, and on account of its simplicity it is certainly one which is very frequently performed.

Ash.

About 1—2 grammes of the sample are ashed in a porcelain crucible over a small flame. To prevent the vapours from catching fire, the crucible is placed in a hole cut in an asbestos board. After the rubber is well charred, it is ignited till the carbon has disappeared. This is most rapidly done in the muffle. Care must be taken that specks of black unignited material are not left under the crust of ash. Ignition should be done at as low a temperature as possible.

It must be remembered that antimony and mercury compounds will be volatilised—as metal, after reduction by the carbonaceous matter. Other substances will lose weight, *e.g.*, magnesium carbonate loses CO_2, and French chalk loses about 5 per cent.

Again, other substances will gain in weight owing to the action of sulphur, etc., which transforms oxides into sulphates.

[1] An extraction with water has been recommended to remove starch, etc. This should clearly be done *before* alcoholic soda treatment. Any extract thus found must be carefully examined.

In this connection, a useful method [1] when oxides are present is to ash the acetone extracted rubber instead of the original sample. Owing to the removal of the free sulphur a better result will be obtained.

Estimation of Mineral Matter by Treatment with Solvents.

A large number of solvents for vulcanised rubber have been proposed for the purpose of this separation. Weber employed hot nitrobenzene, containing 5 per cent. chloroform.

The two chief methods now in use, which are best applied after the acetone extraction, are those of Hinrichsen and his collaborators, and of Marckwald and Frank.

Marckwald and Frank recommend xylene (naphtha). This solvent boils at about 140° C., but they use it in an autoclave at a pressure of 5—6 atmospheres. In this way they claim that complete solution is effected, and that the loss of CO_2 from carbonates is lessened by the pressure applied. The method is undoubtedly ingenious, but, as Hinrichsen and others have pointed out, it requires a long time to heat and to cool the autoclave, and further the use of xylene at these pressures is not altogether free from objection on account of possible explosions. If an autoclave is not available, this operation could, of course, be performed in a sealed tube. The method has not received much consideration in this form, but it has the further advantage that it is easy to inspect the tube (wear goggles during inspection !).

Hinrichsen and his co-workers recommend anisol [2] as solvent, at moderate temperatures. They have also published a method in which high boiling paraffin is used, though others have also used this solvent. Their process is as follows [3]:—

One gramme of dried acetone-extracted rubber is heated in a weighed flask (reflux condenser) with about 25 cub. centimetres of paraffin oil, boiling from 230°—260° C. (this can be obtained by fractionation of kerosene). After complete solution, which may take some time, the liquid is cooled, and diluted with about 75 cub. centimetres benzene. After standing for 24 hours the

[1] W. J. Britland. Private communication.

[2] Anisol is 25*s.* per lb. !

[3] *Chemiker Zeitung*, 1909, 184. Abstract *J. S. C. I.*, 1910, 99.

supernatant liquid is decanted through a tared Gooch crucible with a double filter disc (the crucible should be moistened with the same solvents before being dried and weighed). The filtrate is repeatedly passed through the crucible until it runs through perfectly bright and clear. The precipitate, and also the flask, are well washed with hot benzene, then with light petroleum spirit, alcohol and ether. The flask and Gooch crucible are dried at 100° C. and weighed till constant.

If complete solution cannot be effected with the high boiling paraffin, other solvents can be used, such as camphor oil, etc.

Often the liquid is extraordinarily difficult to filter. In these cases the use of the centrifuge has been recommended.

It has recently been suggested that clear filtrates can be obtained by using a Gooch crucible half filled with "Atmido", a sort of siliceous earth. It does not appear to have been considered whether there is any possibility here of retaining rubber by adsorption.

The mineral matter when finally separated and weighed can be tested for absence of rubber by ignition, when no burnt-rubber smell should be noticed.

Qualitative and Quantitative Examination of Mineral Matter.

If it is desired to make an analysis of the single constituents of the mineral matter, this is usually done on the ash. Volatile mineral matter cannot be estimated in the ash. For antimony and mercury compounds the following method has been proposed by Frank and Birkner[1]:—

Half a gramme of roughly-divided rubber is placed in a round-bottomed flask of 100 to 150 cub. centimetres capacity, 10 grammes ammonium persulphate are added, and then 10 cub. centimetres fuming nitric acid (sp. gr. 1·5). After a few minutes the flask is gently heated on a sand-bath till the vigorous evolution of gas is over. Should any particles of carbonaceous matter remain, 2—3 grammes ammonium persulphate crystals are added in ten to fifteen minutes. The nitric acid is driven off by heat, when a clear colourless melt is obtained. Excessive heat is to be avoided. The flask is cooled, when the contents begin to

[1] *Gummi Zeitung*, 24, 554. Abstract *J. S. C. I.*, 1910, 224.

crystallise. 10 cub. centimetres *HCl* (sp. gr. 1·124) are added, and the liquid is diluted with warm water. After filtration from the insoluble mineral residue, the filtrate is gassed. For technical purposes the precipitated sulphides of antimony and mercury may be freed from free sulphur and weighed. The antimony sulphide can be dissolved out by ammonium polysulphide, the residual *HgS* freed from sulphur by extraction, and weighed.

If antimony sulphide alone is present, it is best transformed to the oxide and weighed as Sb_2O_4.[1] The precipitate is separated from the filter as far as possible and preserved. The remainder adhering to the filter paper is removed by washing with yellow ammonium sulphide. The solution is evaporated to dryness, the main bulk of precipitate is added, and the whole cautiously oxidised by dilute nitric acid, with evaporation to dryness, followed by concentrated and finally fuming acid, with evaporation to dryness. The precipitate is heated and finally ignited to constant weight over the blast. During ignition reducing gases from the flame must not be allowed to come in contact with the precipitate. The crucible is cooled in the desiccator and then for one hour in the balance case, as on account of its size the weight would not be constant otherwise. The object of the manipulation with ammonium sulphide is to avoid the presence of filter paper, which would cause reduction of the oxide, and consequent loss. The precipitate is weighed as Sb_2O_4.

The process works well.

Estimation of Total Sulphur.

This operation is also of great importance, and a very large number of methods have been used. The standard method, as far as accuracy is concerned, is that of Carius, in which the rubber is heated with fuming nitric acid in a sealed tube to a high temperature. The method is troublesome and little used in technical work.

The method of Hinrichsen, of electrolytic oxidation by nitric acid, is a simpler modification. The sample is placed in a small platinum gauze basket, and a current is passed between this

[1] "Analytical Chemistry," Treadwell.

basket and another electrode, both being immersed in nitric acid. If lead or barium compounds are present the residue may be fused with sodium carbonate to remove the sulphuric acid.

It is not proposed to describe all the other methods which have been suggested. Two are in very general use, the peroxide method, and the Marckwald-Frank-Henriques method.

The peroxide method has been largely used in America for the determination of total sulphur in organic compounds. It consists in oxidation by combustion with sodium peroxide. The action is very violent, and methods have been proposed to moderate the reaction by diluting the rubber with salicylic acid, which burns quietly, or by diluting the peroxide with sodium or potassium hydroxide. The great difficulty of applying the method to soft rubbers lies in their coarse state of division, which is a very serious impediment to smooth and quantitative oxidation. In the case of ebonites this difficulty can, of course, be easily overcome. Here the ebonite is mixed with from ten to twenty times its weight of peroxide in a nickel crucible. A layer of peroxide is placed above and below the mixture. The crucible lid is pierced, and the mixture is fired by inserting a red-hot iron wire through the hole. An almost explosive action results. When cool, the crucible is cautiously washed out with water, and the solution is boiled. It is best nearly to neutralise with hydrochloric acid before filtering, otherwise filtration is very slow. The filtrate is acidified with hydrochloric acid, boiled, and precipitated with barium chloride. In this case nitrates are absent, so that the barium chloride should be added, diluted with four volumes of water, and boiling, all at once.

The method which is recommended by the present author is, however, the Marckwald and Frank modification of Henriques' process. This does not appear generally known outside the circle of rubber analysts, but it is a most useful method. With some slight changes in detail the method is as follows:—

The rubber (1 gramme) is treated with 15 cub. centimetres concentrated or fuming nitric acid, if necessary, under the tap. A small conical beaker is used, which is covered with a watch glass or shortened funnel. After *gentle* heating on the water-bath the beaker is finally strongly heated on the water-bath.

The liquid is then transferred to a basin (as in free sulphur estimation) and evaporated down. It has been advised to evaporate finally twice with 3 cub. centimetres fuming nitric acid. This should not be necessary, since all free sulphur should have been oxidised before transference, and it is very difficult to oxidise sulphur in a basin. The same precautions as to moderating this action must be observed, as in the case of free sulphur estimation.

The syrupy mass is then mixed with 5 grammes fusion mixture[1] and cautiously ignited. If lead or barium compounds are present the mass should be fused for a few minutes. After lixiviation with water and filtration, the liquid is acidified with 20 cub. centimetres conc. *HCl* and evaporated to dryness on the hot plate. [Filtration before addition of *HCl* is unnecessary in the absence of lead and barium.] 5 cub. centimetres of dilute *HCl* are added, and the salts are dissolved in water. After filtration, precipitation is effected with about 2 cub. centimetres excess of 10 per cent. barium chloride added drop by drop. The liquid is filtered after a half to one hour. Under these conditions the author has shown that pure sulphuric acid mixed with the salts from blank fusions of pure Para rubber can be estimated to about 5 milligrammes $BaSO_4$ (= 0·07 per cent. *S* on 1 gramme). The results will thus be low by about 0·07 per cent. After standing overnight before filtration the results are not appreciably better. This correction may be used.

If very accurate results are required, it may be advisable to evaporate to dryness with *HCl* several times to remove all nitrates, and precipitate by barium chloride added all at once. The method of precipitation described above is probably the best for general work.

For ebonites, when only 0·5 grammes need to be taken, the fusion can be done with 2 grammes fusion mixture; in this case the author recommends acidification, after fusion, with 10 cub. centimetres nitric acid, evaporation to dryness, addition of 8 grammes *KCl*, precipitation drop by drop (as for free sulphur, see p. 126). This method can also be used for soft rubbers,

[1] If much over 50 per cent. rubber is present, use 10 grammes, with 40 cub. centimetres *HCl* afterwards.

but in that case 20 grammes *KCl* have to be added. The method (of acidification with nitric acid and compensation by *KCl* added afterwards) is, in the present author's opinion, decidedly preferable for ebonites and for free sulphurs, and optional for total sulphurs.

Estimation of Chlorine.

This is usually estimated by heating the finely divided rubber with fusion mixture, finally fusing. The cooled mass is extracted with water acidified with nitric acid, and precipitated by silver nitrate. [A similar method will not suffice for total sulphur, since sulphur is lost.] A blank should be done on the reagents. This method can be applied to the alcoholic soda extract, when substitutes are present, and it is desired to estimate "white substitutes." The extract is evaporated to dryness, and treated as above.

Estimation of Rubber.

The determination of the content of rubber is most difficult. Even if it is performed satisfactorily it does not by any means represent the total amount of rubber originally used in the mixing, since this rubber itself will not contain 100 per cent. rubber substance. The resins are, of course, estimated separately; during vulcanisation they usually increase in amount, and this further complicates a decision as to the amount of raw rubber used, since some of it will have been transformed into matter soluble in acetone. Again, the raw rubber will contain protein. This constituent is usually neglected in the analysis of vulcanised rubber. When the analysis is made by the difference method, protein is included in the percentage of rubber, which, though perhaps scarcely justifiable theoretically, is quite sound from a practical point of view, since we usually desire to approximate as closely as possible to the percentage of raw rubber initially used.

From time to time partisans of the various direct methods for estimation of rubber have made claims which have not been fully substantiated by later work. At the present time, as in the case of raw rubber, we may almost say that the difference

method, in spite of its obvious disadvantages, is in reality the safest and best. That the difference method does not yield results always agreeing with the percentage of raw rubber used does not prove that it is unsound; the discrepancy may be due to deterioration, as a result of which some of the rubber has become soluble in acetone, and is clearly not present as pure rubber.

The nitrosite method has been worked out by Harries, and by Alexander especially for vulcanised rubber. It is long and tedious, and has not been shown to be finally satisfactory, though it may be remarked that the researches of Alexander are characterised by a remarkable degree of care and thoroughness.

Hübener's Method.

Hübener has worked out an extremely simple method for determination of rubber content which deserves some consideration, as although the foundations of the method are somewhat empirical (in the sense that they have not been sufficiently investigated, and when this has been done the underlying principles appear doubtful), it yet appears to yield workable results. In its simplest form his method is as follows :—0·2 grammes rubber (best acetone-extracted) are finely divided, and boiled with a little water in a conical beaker till they are thoroughly wet. A shortened funnel is placed on top of the beaker, which is cooled under the tap. More water, and then 5—10 cub. centimetres bromine are added. The beaker is gently warmed on the sand-bath (or the corner of a hot plate) in the fume chamber. After most of the bromine has slowly disappeared the liquid is heated more strongly and finally boiled. The precipitate is then well broken up. This is best effected by filtering off the supernatant liquid, and powdering the lumpy precipitate in a small basin, with the round end of a thick-walled test tube. After washing, the precipitate is transferred to the beaker, and treated again with 5 cub. centimetres bromine. It should then assume the form of soft flakes. These are broken up as before, and the precipitate, after transference to the filter, is washed well with boiling water till the washings give no precipitate with silver nitrate. The filter and precipitate are transferred to the original

beaker (which may still contain a few specks of precipitate, provided they have been well washed). 20 cub. centimetres conc. nitric acid and 20 cub. centimetres $\frac{N}{10}$ silver nitrate are added. The liquid is boiled down till all the precipitate has disappeared, yielding yellowish silver bromide. If necessary, more nitric acid is added. The liquid is diluted with cold water and titrated with $\frac{N}{10}$ ammonium thiocyanate, using ferric alum as the indicator.

At the same time 0·2 grammes of the original rubber are treated in the same way, except that the filtrate is preserved and the precipitate of tetrabromide is discarded. The filtrate is stated to contain the free sulphur, which is estimated by precipitation with barium chloride, weighing as barium sulphate. The difference between this "free sulphur," and the total sulphur, gives the sulphur remaining in the tetrabromide. [Some remarks on this point will be made later.]

We now know the amount of bromine in the tetrabromide precipitate, from the amount of silver consumed by it (= 20 cub. centimetres less amount of silver found by titration at end). We know also the amount of sulphur in this precipitate. Assuming that in the precipitate the sulphur is attached to the two double bonds of the rubber molecule, and that the bonds unsatisfied by sulphur are satisfied by bromine, we have :—

$$\text{Each atom of } S = \frac{1}{2} \text{ molecule } C_{10}H_{16}, \text{ giving } C_{10}H_{16}S_2.$$

$$\text{(Molec. wt.} = 32) \qquad \left(\frac{1}{2} \times 136\right).$$

$$\text{Each atom of bromine} = \frac{1}{4} \text{ molecule } C_{10}H_{16}, \text{ giving } C_{10}H_{16}Br_4.$$

$$\text{(Molec. wt.} = 80) \qquad \left(\frac{1}{4} \times 136\right)$$

$$\textit{i.e.}, \text{ Rubber} = \left(S \times \frac{136}{2} \times \frac{1}{32}\right) + \left(Br \times \frac{136}{4} \times \frac{1}{80}\right).$$

The calculation is somewhat more complicated when sulphur is present in the mixing as substitute or as antimony sulphide,

or when lead or barium salts are present. We need not discuss these cases further, however.[1]

Hübener has examined in this way a number of rubber mixings of very varied composition, and has obtained results agreeing very well with the percentage of rubber originally added to the mixing. This in itself points to the fact that the results are not really exact, since they ought to be lower than this figure by the amount of resin present.

Apart from this, however, Spence, Galletly and Scott have found that bromine is lost during the conversion of the tetrabromide to silver bromide. They consider that the rubber is brominated excessively, which thus compensates for the loss in boiling with acid. This point also requires consideration in other methods of rubber estimation (cf. p. 64). They recommend heating the bromide with sodium carbonate in a platinum crucible to faint redness, followed by acidification with nitric acid and precipitation with silver nitrate, weighing as silver bromide. A blank is done on the reagents, since small quantities of chloride are often present. If the bromine were estimated by this process in Hübener's method, it seems probable that the result for percentage of rubber would be appreciably high. Nevertheless it is desirable that further investigations should be made.

Various modifications of the method have been proposed by Becker and others. One by Hinrichsen appears worthy of trial, in which the tetrabromide is obtained by treatment with bromine and water, and then purified by solution in chloroform and precipitation with benzine (not benzene), after which it is dried and weighed.

The value for "free sulphur" obtained in this method does not coincide with that obtained by acetone extraction. This may not affect the value for rubber content. Caspari has shown that, contrary to the generally received opinion, the combined sulphur can be attacked by bromine, and that bromine is not a reliable reagent for the oxidation of the free sulphur alone. The present author can confirm the statement that higher values are always obtained by the bromine treatment than by acetone extraction,

[1] For details, see *Chem. Zeit.*, 1909—11; abstracts in *J. S. C. I.*

especially in the case of ebonites. A sample of ebonite which had been extracted sixty hours still yielded a filtrate containing sulphuric acid when treated with bromine in presence of water. This makes it unlikely that "insoluble sulphur" is the cause of the discrepancy; this has not yet been definitely proved, but the universally higher results obtained in Caspari's experiments practically exclude this possibility.

The Axelrod-Budde Tetrabromide Method.[1]

One gramme acetone-extracted rubber is boiled on the reflux (air condenser) with 25 cub. centimetres paraffin (boiling 230°—260° C.) till complete solution has occurred. After cooling, the solution is diluted with paraffin to 100 cub. centimetres. The liquid is well shaken, and 10 cub. centimetres are immediately pipetted out into a beaker containing 50 cub. centimetres of Budde's bromine solution (16 grammes = 6 cub. centimetres Br, and 1 gramme iodine in 1 litre CCl_4). After standing some hours about twice the volume or more of alcohol is added, to "harden" the precipitate (clearly, to coagulate it as far as possible). After further standing, the precipitate is filtered through a tared filter paper and washed, first with a mixture of 2 parts carbon tetrachloride to 1 part alcohol, and finally with alcohol alone. It is then dried till constant at 50°—60° C. A drop of conc. sulphuric acid is added, and the precipitate is ashed. The weight of mineral matter thus obtained is deducted from the weight of precipitate. As Hinrichsen has pointed out, this method of working leads to errors, but usually for normal mixings these are not serious.

$$\text{Rubber} = \text{precipitate} \times 0{\cdot}314.$$

(The factor is an empirical one, obtained as the result of experiments with mixings of known composition.)

The author prefers to use a Gooch crucible for the filtration; ashing can be done without the asbestos losing weight, provided that this is good and well-purified.

This method tends to give results which are decidedly too low.

On the whole, here, as in the case of raw rubber, it must be

[1] *Jahrbuch der Kautschuk Industrie.*

admitted that, to the present, the difference method is really the safest, provided that due care is exercised, and that a small amount is allowed for solubility of the rubber in certain solvents, *e.g.*, about 0·5 per cent. in alcoholic soda.

Determination of the Coefficient of Vulcanisation.

This ratio is obtained by expressing the sulphur combined with the rubber as a percentage on the rubber present. It is one of the most valuable analytical results. When no sulphur is contained in the organic and mineral fillers, the estimation is simple. The combined sulphur is then equal to the sulphur of vulcanisation, and is obtained by difference between the free and total sulphur, or is estimated directly on the acetone-extracted rubber. If substitutes are present it is best to estimate the sulphur of vulcanisation on the dried sample after the alcoholic soda treatment, and to calculate the result on the original rubber. If mineral matter containing sulphur is present, such as lead or barium compounds, it is necessary :—(1) To estimate the combined sulphur and then to estimate the sulphur in the mineral matter after removal of the rubber by paraffin oil; the difference between the results gives the sulphur of vulcanisation, or (2) To separate the rubber from the mineral matter by solution in a solvent such as xylene under pressure, to isolate the rubber from the solution by distillation in steam, and then to estimate the sulphur of vulcanisation directly in the rubber. This method has been used by Seidl; as an alternative to (1) it is worthy of note.[1]

A third method which has been used is that of obtaining the tetrabromide or the nitrosite, and estimating the sulphur in the product. It was considered that the sulphur of vulcanisation passed quantitatively into these derivatives. This is doubtful; in the case of the tetrabromide it has been definitely disproved by Caspari and by Esch (see p. 143, for the cases when bromine is used in water and also in carbon tetrachloride). It is therefore unnecessary to discuss these methods further.

[1] For details of method, see *J. S. C. I.*, 1911. It may be added that according to the recent work of Bary and Weydert the combined sulphur is probably diminished by this treatment.

Durability.

A method which is absolutely satisfactory for testing the durability of vulcanised rubber has yet to be devised, short of actual exposure to deteriorative influences for a lengthy period. Shorter methods are used however. Thus the samples are often exposed to the action of mineral oil, acetic acid and other reagents.

Weber recommended immersion for two days in a mixture of hydrogen peroxide and acetone (at least a fortnight old). The gain in weight represents oxidation. Ditmar has used a method in which the samples are heated at 100° C. in oxygen. Some samples gain in weight, while others lose, owing to loss of free sulphur. It would probably be advisable to supplement the mere weighing before and after heating in oxygen by determination of acetone extract before and after. This modification does not appear to have been suggested hitherto. Mere lapse of time does not necessarily mean that the acetone extract will increase, as the present author found that two mixings, samples of which had been cured for a number of different times, gave quite normal acetone extracts after keeping in the dark for a year. It is not certain that deterioration is always accompanied by increase in acetone extract, though the oxidation products which have been isolated are certainly soluble. It seems likely that the method suggested might furnish some measure of the liability to decompose, from the difference in acetone extract before and after oxidation.

LITERATURE.

"The Chemistry of India Rubber," Weber; "Analyse des Kautschuks," Ditmar; "L'Analyse du Caoutchouc," Pontio; a section of "Allen's Commercial Organic Analysis," by E. W. Lewis; "Der Kautschuk und Seine Prufung," Hinrichsen and Memmler. In the latter an extremely exhaustive discussion of the mechanical tests will be found. More information on this point is contained in "Rubber," Schidrowitz, and in "The Rubber Industry," the report of the International Rubber Congress of 1911, in which are published papers on the subject by Memmler, and by Beadle and Stevens. The paper of Schwartz (Abstract *J. S. C. I.*, 1910), may also be consulted. Frequent papers on analysis will be found in the journals.

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